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THE PHYSICAL REVIEW

VOLUME 43 *Second Series* NUMBER 3

FEBRUARY 1, 1933

Published for the

AMERICAN PHYSICAL SOCIETY

by the

AMERICAN INSTITUTE OF PHYSICS
Incorporated

LANCASTER, PA., AND NEW YORK, N. Y.

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THE PHYSICAL REVIEW, which was established in 1893, is a journal of experimental and theoretical physics. It is published for the American Physical Society by the American Institute of Physics Incorporated. There are four volumes annually with six issues in each volume.

Manuscripts for publication should be submitted to John T. Tate, University of Minnesota, Minneapolis, Minnesota.

Proof and all correspondence concerning papers in the process of publication, should be addressed to the Editorial Secretary, American Institute of Physics, 11 East 38th Street, New York, New York.

Subscription price $15.00 per year. Single copies $1.50 each for issues prior to July 1, 1929 (Vols. 1–33); $.75 each for issues subsequent thereto. Subscriptions and orders for back numbers should be addressed to Prince and Lemon Streets, Lancaster, Pennsylvania, or to the American Institute of Physics, 11 East 38th Street, New York, New York.

Advertising is not accepted for the *Physical Review* but attention is called to the *Review of Scientific Instruments* with *Physics News and Views*, a companion publication of the Institute, and a medium through which the field of physics can be reached most effectively. Rates and other information will be furnished on request to the Editorial Secretary.

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The Physical Review is published semi-monthly at Prince and Lemon Streets, Lancaster, Pennsylvania.

Entered at the Post Office at Lancaster, Pennsylvania, as second class matter.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized September 6, 1926.

THE
PHYSICAL REVIEW
A Journal of Experimental and Theoretical Physics
VOL. 43, NO. 3 FEBRUARY 1, 1933 SECOND SERIES

The Electrostatic Production of High Voltage for Nuclear Investigations

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(Received December 20, 1932)

The developments in nuclear physics emphasize the need of a new technique adapted to deliver enormous energies in concentrated form in order to penetrate or disrupt atomic nuclei. This may be achieved by a generator of current at very high voltage. Economy, freedom from the inherent defects of an impulsive, alternating or rippling source and the logic of simplicity point to an electrostatic generator as a suitable tool for this technique. Any such generator needs a conducting terminal, its insulating support and a means for conveying electricity to the terminal. These needs are naturally met by a hollow metal sphere supported on an insulator and charged by a belt conveying electricity from earth potential and depositing it within the interior of the sphere. Four models of such a generator are described, three being successive developments of generators operating in air, and designed respectively for 80,000, 1,500,000 and 10,000,000 volts, and the fourth being an essentially similar generator operating in a highly evacuated tank. Methods are described for depositing electric charge on the belts either by external or by self-excitation. The upper limit to the attainable voltage is set by the breakdown strength of the insulating medium surrounding the sphere, and by its size. The upper limit to the current is set by the rate at which belt area enters the sphere, carrying a surface density of charge whose upper limit is that which causes a breakdown field in the surrounding medium, e.g., 30,000 volts per cm if the medium is air at atmospheric pressure. The voltage and the current each vary as the breakdown strength of the surrounding medium and the power output as its square. Also the voltage, current and power vary respectively as the 1st, 2nd and 3rd powers of the linear dimensions.

INTRODUCTION

ANY basic development in science calls for a new technique fundamentally adapted to the new purpose. Such a basic development has been in progress for the last thirty-six years and it has now reached such a stage as to be recognized as a major field of physics,—nuclear physics. To justify this statement it is only necessary to point out that in the atomic nuclei reside all the positive electricity, much of the negative electricity and by far the greater part of the mass and energy in the universe. As yet we know relatively little about this world of electricity, mass and energy, and our attempts to produce an impression on it have been still less successful. Nevertheless, recent years have demonstrated the possibility of successful attack upon the nucleus by one weapon, the high-speed particle. The new technique which is therefore demanded is a powerful, controllable source of high-speed particles. In this paper is described a high-voltage generator which, with accessory discharge tubes and sources of ions, appears adapted to this technique.

Since progress in this new field of nuclear physics will require a great investment in apparatus, time and effort, it is important to consider carefully the possible techniques and whether this investment may be justified by the

* National Research Fellow at Princeton from September 1929 to September 1931.

importance of the results to be expected. This leads to a consideration of the effects on the progress of physical theory of basic experimental developments initiated at the close of the last century.

About 1895 the discovery of x-rays and other experimental developments made possible an effective entry into the outer structure of the atom and the investigation of this aspect of atomic structure has been the main business of physics since that time. The distinguishing feature of those experimental innovations which led to the present knowledge of the outer atom is that they made possible physical observations on a scale of dimensions thousands of times smaller, with resultant energy concentrations thousands of times larger than were previously possible. Thus it became possible to deal individually with the basic physical entities, thereby removing the limitations of the statistical approach formerly necessary. Such observations showed clearly the insufficiency of classical laws and paved the way for quantum theory and for relativity.

Just as x-rays and other radiation phenomena of extranuclear electrons unfolded for us the extranuclear structure of atoms, so the discovery of radioactivity in 1896 opened the way to the first knowledge of the inner structure of the atomic nucleus. Furthermore, the high-speed particles from radioactive substances have themselves been the agencies through which was obtained the first evidence of the possibility of atomic transformation. Simultaneously with these experimental developments, the theory of relativity, through Einstein's principle of interconvertibility of mass and energy, has given a partial basis for guidance in interpretation and investigation of nuclear changes. These developments in nuclear physics have suggested with increasing emphasis the tremendous possibilities which should accrue from further development in the technique of nuclear investigation, through the use of swift particles of controllable nature and speed produced and applied through the agency of high voltage. In fact, the recent brilliant experiments of Cockcroft and Walton[1] have given concrete evidence that these expectations were justifiable.

[1] Cockcroft and Walton, Nature **129**, 649 (April, 1932); Proc. Roy. Soc. **A137**, 229 (1932).

It may be hoped that experimental entry into the nucleus will extend the technique of physical exploration in a manner analogous to the extension which opened up the outer structure of the atom. It will again be possible to study a system thousands of times smaller, with energy concentrations correspondingly greater, further facilitating the study of individual rather than statistical processes. This may result in a system of nuclear mechanics accompanied by the same sort of broadening of basic scientific and philosophical ideas as accompanied the creation of quantum mechanics.

Within the almost unknown nuclear world of electricity and energy may also lie the explanation of certain extranuclear phenomena, which, modern quantum theory notwithstanding, still remain obscure. Just as the discovery of nuclear charge led immediately to the interpretation and simplification of that complicated group of chemical phenomena partially classified by the periodic table, so similarly it is possible that further discoveries regarding the atomic nucleus may lead to a similar interpretation and simplification of some extranuclear problems still outstanding.

Production of High Voltage

In approaching the problem of a high-voltage technique fundamentally adapted to meet the new demands in the most perfect and ultimate manner, it is well to review the development of the high-voltage art to its present state.[2] Before the time of Faraday electrostatic generators were employed. However, industrial developments of the past hundred years have found their most suitable embodiment in applications of Faraday's principles of electromagnetism. Thus modern high-voltage technique has evolved almost completely under this influence. Step-up transformers have been used, with the addition of rectifiers and condensers when an approximately steady direct current was desired. These electromagnetic devices are admirably suited for the production

[2] Lack of space prevents discussion of methods now used for generating high-energy radiations, but reference may be made to such well-known work as that of Coolidge, Tuve, Lauritsen, Cockcroft and Walton, Brasch and Lange, and Lawrence, and their collaborators.

of large currents within the general range of voltages corresponding to extranuclear phenomena. There are, however, inherent difficulties in the extension of such devices into the range of extremely high voltages which are demanded by nuclear physics. Such difficulties include the tremendous expense and size of such generators, necessitated by insulation requirements. There is also the limitation that the efficiency of high-voltage a.c. devices decreases rapidly as higher voltages are sought, because of the parasitic charging currents which are required to bring the apparatus to high potential at every cycle, even though no power is being drawn by it. The importance of this feature is not generally realized, but may be illustrated by the statement that the most favorable arrangement of the two terminals alone, neglecting the circuits, would require about 10,000 kva to impress 10,000,000 volts at 60 cycles, exclusive of useful output or corona leakage.

There are, in addition, numerous other important advantages of steady direct current over any current of a surging, alternating or rippling character. These include:

(1) Possibility of obtaining strictly homogeneous beams of electrified particles.

(2) Possibility of accurate focussing which becomes relatively more important as the voltage and therefore the length of discharge tubes is increased.

(3) Elimination of stray radiation which arises in a variety of ways from a discharge tube and generating apparatus operating at unsteady voltages, and which renders difficult the careful shielding necessary to permit the use of the delicate instruments and sensitive amplifiers required in so many applications of these voltages.

(4) Ability to use the ion source to full capacity since the useful voltage is applied all of the time. (The order of advantage in this respect runs from the impulse generator and Tesla coil, which utilize the source only during roughly a millionth of the time, through the induction coil, the a.c. transformer, the transformer with rectifier, to finally, the electrostatic d.c. generator.)

(5) Ability to measure the high potentials accurately as, for instance, by the use of null or compensation methods.

(6) Elimination of breakdown in vacuum tubes due to reversal of the voltage,—a phenomenon inherently associated with the walls of vacuum tubes even under the best available conditions of evacuation.

(7) Ability to utilize the advantages of geometrical dissymmetry between positive and negative electrodes in vacuum in such a way that the field is minimum at the surface of the negative electrode, where difficulties from field currents are most serious,—an advantage which finds its maximum embodiment when the cathode is a hollow sphere surrounding a central spherical anode.

(8) In a variety of other ways through the elimination of time variations in the electrical conditions of the apparatus.

In view of these considerations it seemed desirable to develop an electrostatic high-voltage generator, since electrostatic methods yield directly a steady unidirectional voltage such as is desired. Maximum simplicity was sought in the design. The simplest terminal assembly appeared to be a sphere mounted on an insulating column. Since the sphere must be charged and since the process should be continuous the charge carrier should approach the sphere, enter it, and, after depositing its charge inside should return parallel to its path of approach. This immediately suggested the action of a belt, a device long used for the transmission of mechanical power.

The logic of the situation therefore pointed directly to a generator consisting of a hollow spherical conducting terminal supported on an insulating column, a moving belt to carry electric charge to the sphere, a device for depositing the charge onto the belt in a region of low potential remote from the sphere, and a device for removing this charge from the belt inside the sphere and transferring it to the sphere. A refinement of these essentials was the addition of an induction device whereby charge of the opposite sign was carried by the belt on its return journey, thus doubling the current output. A second refinement consisted of a self-exciting charging device whereby the entire generator could be made to operate independently of any external source of electricity. Not only does this device attain the desired result in what appears to be the simplest possible manner, but it is also interesting to note that the energy transformations in its operations

are exceedingly simple, consisting only in the transformation of the energy required to drive the belt into work done in separating and transferring electric charge from earth potential to sphere potential.

Historical note

The basic idea of a belt type of generator probably dates from Kelvin's famous water dropper,[3] and in fact, Kelvin suggested such a generator, in which charges would be carried to the electrode on a belt conveyer consisting of alternately insulated metal segments. Righi[3] made such a generator with the segmented belt carried through the sphere. Later Burboa[4] designed a generator with a belt functioning somewhat as an elongated disk of a Wimshurst machine, with a complicated set of inductors and brushes. Mention also should be made of a generator designed by Swann,[5] in which charge was conveyed by a succession of falling metal spheres, thus coming closer to Kelvin's original water dropper but with the added suggestion that this apparatus could be made to operate in vacua theoretically up to such voltages as would prevent the falling of the spheres by electrostatic forces. Still more recently Vollrath[6] constructed a similar generator in which the current is carried by an air blast of electrified dust in an insulating tube.

Principles of Operation

The simplest embodiment of these principles is illustrated schematically in Fig. 1, which is appropriate to a generator, where P and N are the positive and negative spherical terminals and the belts of silk, or any other flexible insulating material, are shown transporting positive and negative electricity, respectively, from the charging outfit connected with ground to the two spheres. The charge is "sprayed" onto each belt as it passes between a metallic surface and one or more sharp points so adjusted as to maintain a brush discharge from the points toward the surface. When connected as shown, one point sprays positive and the other sprays negative electricity onto its adjacent belt. Within each sphere the charge is drawn off the belt by adjacent sharp points and transferred to the spheres. Since the interior of the sphere is similar to the interior of a Faraday "ice pail" the charge passes readily between the charged belt and the sphere, irrespective of the potential of the sphere.

The voltage which is attainable in this device is limited only by the corona breakdown at the surface of the spheres, which depends in a known manner upon their size and varies somewhat with the degree of smoothness of their surfaces. The current output is equal to the rate at which charge is carried into the spheres and is therefore

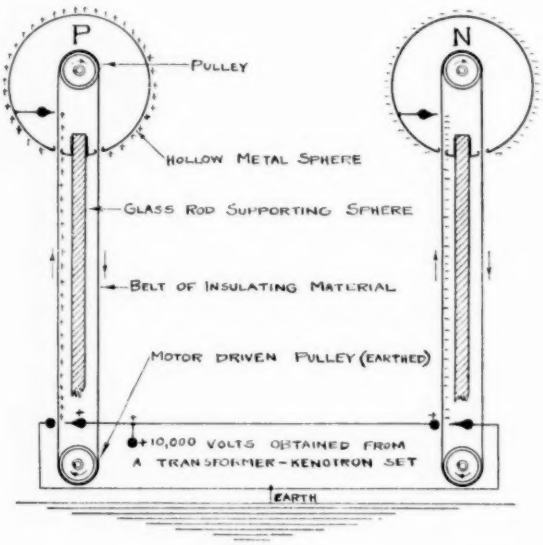

Fig. 1.

equal to the product of the surface density of charge on the belts multiplied by the areal velocity with which the belts enter the spheres. The upper limit for the surface density of charge on the belts is that which gives rise to an electric field equal to the "breakdown" strength of the surrounding air.

It is evident that other insulating media than air at atmospheric pressure might be used to advantage in the operation of such a generator.[7] We believe that its most useful embodiments will prove to be with operation in a high vacuum

[3] John Gray, *Electrical Influence Machines*, Whittaker, London, 1890.

[4] Burboa, U. S. Patent Nos. 776,997 (1904).

[5] Swann, J. Frank. Inst. **205**, 820 (1928).

[6] Vollrath, Phys. Rev. **42**, 298 (1932).

[7] Barton, Mueller and Van Atta, *A Compact High-Potential Electrostatic Generator*, Phys. Rev. **42**, 901A (1932).

tank. In any case, the voltage is limited by the electrical breakdown of the surrounding medium whatever it may be, and the current output is determined by the width and velocity of the belt together with the charge density which can be placed on it.

In view of these considerations it is evident that the maximum voltage and also the current of such a generator each vary directly as the breakdown strength of the surrounding medium, so that the power output varies as the square of this breakdown strength. Since generally it will be desirable to provide as large a current output as possible, the belts will be designed to operate at the greatest practicable speed, and multiple belts will be placed as closely together as convenient. It is therefore evident that in any given insulating medium the voltage will vary as the first power, the current as the second power, and the power output as the third power of the linear dimensions. The variation of current with the square of linear dimensions is evident when it is considered that any increase in dimensions permits a corresponding increase in belt width and also a corresponding increase in the number of belts which can be introduced to operate in parallel.

In adapting the design of Fig. 1 to operate in some other medium, such as in a vacuum or in a liquid, it is only necessary to replace the brush discharge method of introducing charge to and from the belt, by some other charging and discharging device appropriate to the medium. Under such conditions it may also be advantageous to construct the belt of alternate conducting and insulating segments.

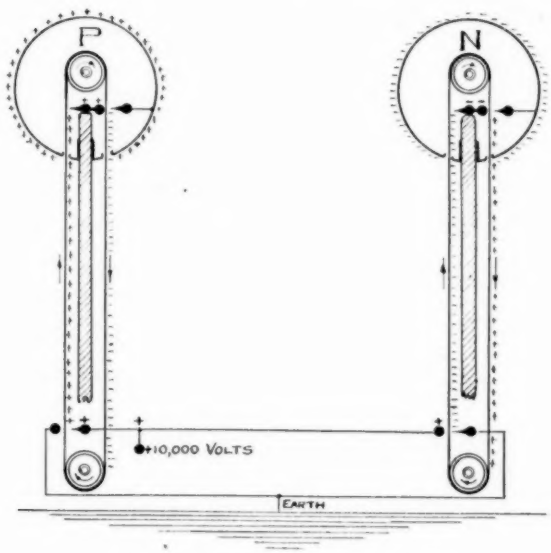

FIG. 2.

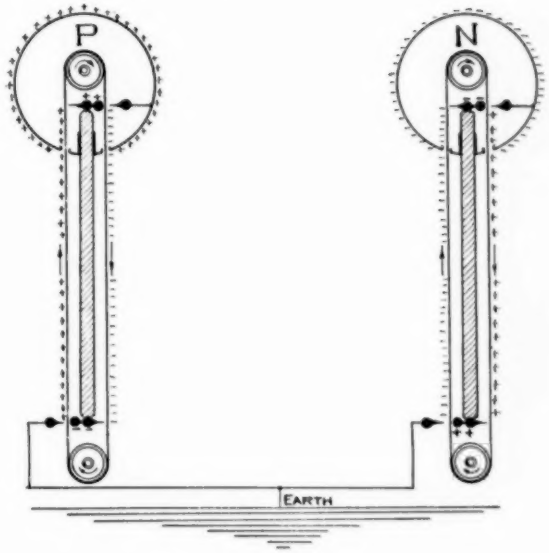

FIG. 3.

It is obvious that the current output of this device can be doubled if the belt on its passage out of the sphere can carry away a charge equal and opposite to that brought in by the incoming belt. This can be realized very simply through the separation of induced charges by the arrangement which is shown schematically in Fig. 2. This exemplifies the first refinement referred to in the preceding section.

The second refinement there mentioned is illustrated in Fig. 3, in which the transformer-kenetron set which charges the belts is omitted and the connections are made in such a way that a small charge on the moving belt, such as is present due to friction of the belts and pulleys, results in the cumulative separation of positive and negative electricity by induction, thus priming the machine, which immediately begins to operate self-exciting and at full power, in this way dispensing with the necessity of any external electrical connection.

PRELIMINARY MODELS OF THE GENERATOR

(1) In 1929 a small model was constructed and used to demonstrate the soundness of the principles involved. This model was hastily impro-

vised but performed as expected. The highest voltage obtained was about 80,000 volts, being limited by the electrical breakdown of the surrounding air.

(2) Following this there was constructed a larger generator contained in a dismountable tank which could be highly evacuated by a suitably designed combination of high-speed mercury condensation pump and liquid air trap. This type of generator is still in the stage of development but has operated in vacuum at 50,000 volts. Progress has been slow due to the necessity of developing certain necessary points of vacuum technique, and also due to the fact that this work had to be temporarily discontinued for the past eighteen months. However, no unexpected difficulties have been encountered and it is hoped that this generator will be in successful operation in a few months. Thus far experience has confirmed our confidence that vacuum insulation is the ultimate insulation for electrostatic devices and will open up tremendous possibilities in this field.

(3) When it became evident that considerable work would still be required to perfect the vacuum generator, construction was begun in June, 1931 of a generator operating in air, powerful enough to be of scientific use and to give a demonstration of the possibilities of generators of this type. This generator was designed for and developed about 1,500,000 volts and delivered a current of about 25 microamperes. It was constructed with 24-inch spherical electrodes mounted on 7-foot upright Pyrex rods and charged by 2.2-inch silk ribbon belts moving with a linear speed of 3500-foot per minute, and it operated either by self-excitation or by the spraying on of charge from a small 10,000-volt transformer kenetron set. It is interesting to note that although it was constructed at a total cost for materials of only about $100 it developed approximately twice the voltage of any previous direct-current source of which we have knowledge. This generator was described[8] at the Schenectady meeting of the American Physical Society in September, 1931.

Current output

If a charge is uniformly distributed on the surface of a linear strip in a region otherwise free from electrical forces, there is set up a field perpendicular to the strip and proportional to the surface density of charge as given by Coulomb's law. The maximum charge which can be held by the strip is that which gives rise to a field equal to the breakdown strength of the surrounding insulating medium. In the case of air this limiting field is about 30,000 volts per centimeter, from which we calculate that the maximum charge on a belt in air amounts to 2.65×10^{-9} coulombs per sq. cm on each side of the belt. This figure when multiplied by the number of sq. cm of belt surface which enter the sphere per second, gives the maximum possible current output in amperes. Of course, this current output will be doubled if the belt leaves the sphere also fully charged, but with electricity of opposite sign. In the generator described above as preliminary model 3, the actual current output amounted to about one-fourth of this theoretical maximum. The reasons for this discrepancy were known at the time, but were neglected in the construction of this demonstration model. By more careful design, the output may be brought closer to the theoretical limit, as more recent tests have shown.

There are several factors which account for this inability to attain ideally maximum current output. (1) Only one side of the belt is "sprayed" with charge. This may be overcome by using, for example, a double layer belt split by an earthed metal separator between two sets of converging spraying points and traversing the rest of its path simply as a 2-ply belt charged on both outside surfaces. (2) There are inevitable irregularities in the surface, and the breakdown of insulation in those regions which are electrically overstressed, results in a diminution of the charge carried in those localities. (3) There is an additional component to the electric field arising from the difference in potential between the sphere and the earth, so that the electric intensity at any point is the vector sum of this field and that arising from the charge of the belt. A nonlinear potential distribution along the belt may result in overstressing of the insulating medium in the region just outside the sphere, resulting in failure of the belt to retain its maximum charge while traversing that region. This difficulty is obviated by the use of a supplementary device for insuring uniform potential distribu-

[8] Abstract, Phys. Rev. 38, 1919 (1931).

tion, as described below. (4) Of course the charging device must be adequate to supply the charge. With a wide belt, a multiplicity of spraying points may be necessary to insure complete and adequate coverage. (5) If the belt is charged by a brush discharge, as in this model, the surrounding air is of course partially ionized, and this condition tends also to reduce the charge which can be placed on the belt by reducing the breakdown strength of the air in the charging locality to some value less than 30,000 volts per cm. This limitation could be removed by use of a non-ionizing device for charging the belts. The brush discharge method of charging, however, has the great advantage of simplicity.

It is impossible to increase the charge carrying capacity of the belt by any change in distribution of charge within the belt, such as by the substitution of volume charges in a moving element for surface charges. This is due to the fact that the limit to the net charge is set by the field just outside the surface of the moving element and is thus independent of the distribution of charges within it.

A consideration of the nature of the limiting electric field around the belts shows that the ascending and descending belts may be placed as close together as desired without reducing their current carrying capacity, the limitation being set only by mechanical considerations such as friction. For this reason it is possible to introduce multiple belts, alternately ascending and descending and packed very closely together and so to increase the current output to quite large values.

Efficiency

The work involved in operating this generator is consumed in overcoming the friction of the pulleys and the resistance to the motion of the belt in the surrounding medium, and in the transference of electric charge from earth potential to the potential of the spherical terminals. As is well known, a belt is one of the most efficient means of transferring power, and the two inherent types of electrical losses may be reduced to very small amounts. The first of these arises from electrical leakage, which may be controlled and reduced by methods described in the next section. The second is loss in the process of charging and discharging the belts, which may be reduced to that corresponding to the voltage required to maintain corona discharge from the spraying and discharging points, a voltage which is insignificant in comparison with the voltage generated. There are of course no magnetic losses. Thus this type of generator should be capable of operation with high efficiency.

Disturbing factors

The only disturbing factor which has been found to affect the satisfactory operation of the generator is electrical leakage which is closely identified with two factors, humidity and geometrical design of insulating support. The difficulty is not so much from direct electrical loss by leakage over the surface of the support, as from distortion of the electric field about the spheres by the charges which leak down the supporting insulator and in this way promote insulation breakdown of the air surrounding the insulator near where it enters the sphere. This disturbing factor is completely eliminated by proper design of the insulating support, consisting in the substitution of a hollow insulating cylinder for the insulating rod of model 3. The interior of this cylinder can be maintained at low relative humidity by warming the air within it, so that its interior and exterior surfaces, as well as the belts which run within it, are maintained in the most favorable conditions for elimination of leakage. In addition to improving insulation, the cylindrical support introduces increased mechanical strength, quietness of operation and safety, and certain other advantages.

A number of important advantages are secured by introducing on the surface of the supporting cylinder an artificial leak from the sphere to the ground, so constructed as to give the most favorable distribution of field between the sphere and the earth. This artificial leak may be constructed, for example, by rotating the cylinder in a lathe and drawing on its surface a continuous, closely spaced, helical, India ink line, extending from one end to the other. By means of this artificial leak the vertical field between the earth and the sphere may be made uniform, thus minimizing leakage to earth through the support or the surrounding air, and permitting the maximum charge to be carried by the belt throughout its entire path.

The Large Generator under Construction at Round Hill

The favorable experience with the preliminary models described above appeared to justify the construction of a generator capable of yielding the maximum performance which can reasonably be expected in a generator operating in air, subject to limitations in voltage set by the size of the building in which it is placed. The generator was therefore designed to take full advantage of the largest laboratory space available, which was the airship dock on the estate of Colonel E. H. R. Green, kindly put at our disposal for this purpose. This dock is a building of structural steel covered by corrugated sheet metal and has dimensions approximately $140\times75\times75$ ft. In the back end of this building a row of low rooms has been erected to serve as shop and office headquarters, while running lengthwise down the middle of the floor space there has been installed a railroad track of 14-ft. gauge, extending through the huge doors at the front of the building out into the open air for a distance of 160 ft. On this track each of the two generating units is mounted on a truck of structural steel, so that their distance may be varied and they may be run out-of-doors for experiments in the open air. In this connection it is interesting to note that Round Hill is extremely exposed to fogs from the ocean, so that the experience with this generator will afford a severe test of the utility of an electrostatic device under adverse conditions.

A schematic view of the large generator is given by Fig. 4. Its detailed description will be postponed to include its performance tests, but the following information may be of interest.

The spheres are of aluminum alloy 15 ft. in diameter with walls ¼-inch thick. They were pressed and shipped in "orange peel" sections which were then welded together, and the outer surface ground and polished. Each sphere has four circular holes; a six foot hole on the bottom admits the multiple belts; a trap door on the lower side permits entrance via a ladder from the ground; a trap door on top permits access to the top of the sphere; a trap door on the equator will admit the end of a large discharge tube, spanning the gap between the spheres, to project within the sphere for attachment of subsidiary apparatus and connections and for operation. Preliminary tests on such a discharge tube have been made.[9] The inside of each sphere is itself a laboratory room, provided with a floor and containing accessory apparatus.

The insulating supports are cylinders of Textolite about 24 ft. high, 6 ft. in diameter and of ⅝-inch wall thickness. Each cylinder consists of three 8-foot sections, joined by internal Textolite bands fastened with Textolite dowel pins. Thus the external surface is smooth for easy application of the artificial surface leak and there is an absence of intermediate metal parts, as their presence would distort the field.

The trucks are made of structural steel and are so designed as to permit easy access to or change of the assembly of motors, pulleys and belts.

These three elements, sphere, insulating support and truck, are fundamental elements of any high-voltage assembly, and permit complete freedom for future experimentation and further development of the devices for generation. At the time of writing the spheres are built and polished, the trucks are completed and the main structure is now being assembled.

The spheres were supplied by the Chicago Bridge and Iron Works and the Textolite cylinders (Shellac Compound, No. 974) by the General Electric Company, both of which organizations have been very cooperative in their efforts to make the generator successful.

On the basis both of theory and of past experience, we expect this generator to develop about 10,000,000 volts. The power output will depend on the number, size and speed of the belts. Present plans are for an output of about 20 kw. This could be greatly increased by the installation of additional belts, but for the initial adjustments only a portion of this power will be required.

Without the cooperation of many people this project could not have been carried through to its present state. It is impossible to make all the acknowledgments which are due, but we cannot let the opportunity pass for expressing the following acknowledgments.

We wish to express our great indebtedness to

[9] Van Atta, Van de Graaff and Barton, Phys. Rev. **43**, 158 (1933).

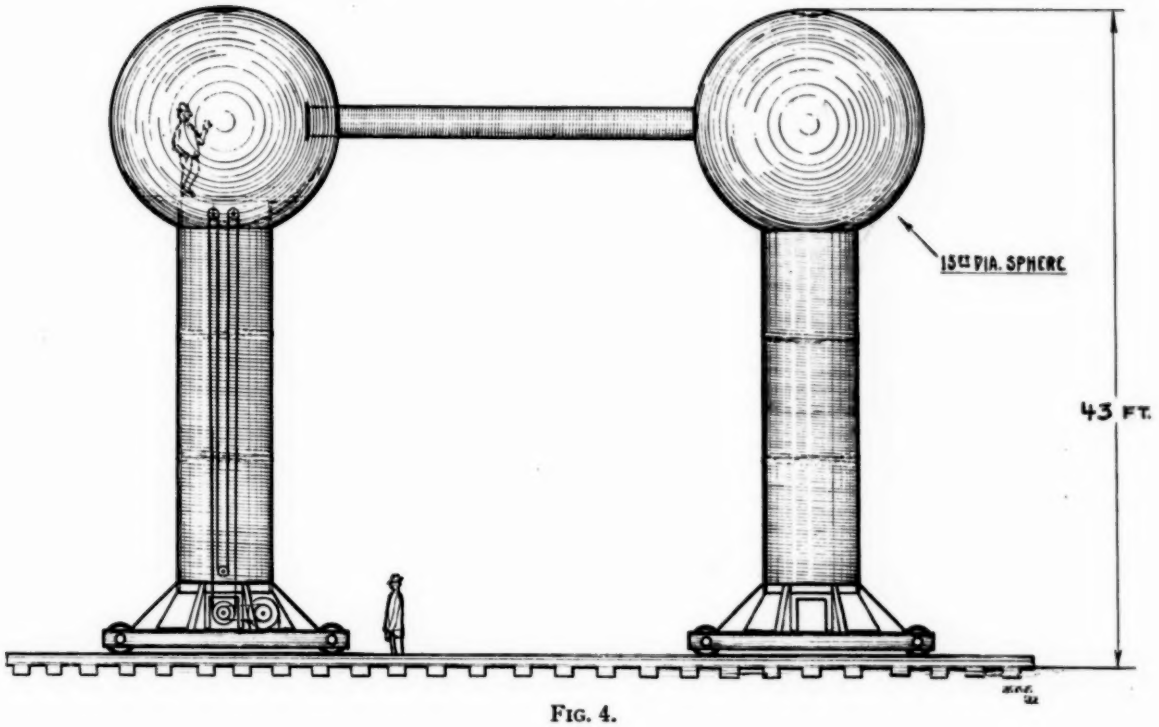

FIG. 4.

the Research Corporation of New York for a grant defraying a considerable portion of the expenses involved in the construction of this large generator, and for the great interest and help which its officers have given in the development of the engineering plans and the carrying through of the entire project up to the point of assembly.

This new high-voltage installation will be a significant addition to the facilities for scientific and engineering research in the Experiment Station of the Massachusetts Institute of Technology which is operated, with the generous cooperation and support of Colonel E. H. R. Green, on his estate at Round Hill. We wish particularly to thank him for his permission to transform the airship dock, equipped with electric power and other services, into a high-voltage laboratory.

We are also greatly indebted to the New York, New Haven and Hartford Railroad for their donation of the railroad track.

Many of our colleagues have been very kind in their assistance. We wish particularly to mention Professor E. L. Bowles who is in supervisory charge of M. I. T. operations at Round Hill.

We wish finally to acknowledge the kind cooperation of Princeton University in whose Palmer Physical Laboratory the preliminary models of this generator were built, and which sponsored the project up to the time when the new facilities at Round Hill became available.

A New Design for a High-Voltage Discharge Tube

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and
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(Received December 20, 1932)

A description is given of tests with a high-voltage tube of simple and rugged design. The tube consists essentially of a fiber cylinder extending between the electrodes and evacuated to a pressure of 4×10^{-6} mm Hg during operation. A potential of 300,000 volts could be maintained on a section of tube 53 cm long. In spite of the fact that the voltage was limited by discharge there was no case of puncture. A simple clear-cut mechanism for the initiation of discharge in vacuum (independent of field currents) is given together with confirming experimental evidence. On this basis there is proposed a method of screening the electrodes to prevent breakdown and permit the application of extremely high voltages to the tube.

CERTAIN high-voltage generators of recent design[1, 2] have made desirable a new type of vacuum tube to be used in conjunction with them. To meet the electrical and mechanical requirements we have developed a vacuum tube consisting essentially of an insulating fiber cylinder, with a helical high-resistance leak, mounted between the high-voltage electrodes. Electrically it thus provides a uniform potential gradient in a cylindrical vacuum space between flat terminal electrodes. Great mechanical strength is obtained by the use of a cylinder of laminated paper impregnated with shellac and securely fastened to metal terminal sections. Such construction permits of extending the size to large dimensions. The experimental development of this type of tube has encountered no serious difficulties and has yielded interesting information.

The voltage source for this preliminary experimental work was a belt electrostatic generator having 24-inch terminal spheres.[3] A fiber cylinder (Textolite, shellac composition No. 974, manufactured by the General Electric Company) 7 inches in diameter and with a ¼-inch wall was mounted between the spheres. A leakage resistance of about 3×10^{11} ohms along the surface was provided by a helical india ink line drawn with 3 turns to the centimeter while the cylinder was rotated in a lathe. A thin coating of ceresine protected the tube and ink line against moisture. The ends of the tube were capped with metal disks. Vapor pressure was effectively reduced by a large liquid air trap placed directly in the tube but outside the path of the discharge. In the presence of a discharge the pressure built up to 4×10^{-6} mm as measured on an ionization gauge. After some preliminary trials a potential difference of 300,000 volts was maintained on a 53 cm length of tube.

There was no instance of electrical puncture in the tube in spite of prolonged operation with the voltage limited by discharge. Even efforts to cause puncture by sliding a sharp grounded electrode along the tube produced no disruptive effect. There were several factors tending to eliminate puncture:

(1) The stored energy of the generator was small since its electrostatic capacity was only that of its spherical electrodes.

(2) The voltage source was limited in current to 40 microamperes, and could be reduced by controlling the rate of spraying on the belt.

(3) The helical ink line imposed on the tube and the flat electrode surfaces a uniform gradient of 6000 volts per cm, thus substantially eliminating field currents. In this connection it is interesting to note that the uniformity of the field makes possible accurate control and focussing of the ion beams.

[1] Van de Graaff, Compton and Van Atta, Phys. Rev. **43**, 149 (1933).

[2] Barton, Mueller and Van Atta, Phys. Rev. **42**, 901A (1932).

[3] Van de Graaff, Phys. Rev. **38**, 1919A (1931).

(4) The conductivity of Textolite, being much greater than that of glass, prevented the building up of a disruptive potential difference across the wall of the tube due to the drift of ions.

Since the voltage across the tube was current-limited, a number of tests were made to determine the nature and source of the current:

(1) An attracted-disk voltmeter placed near one of the high-potential spheres showed a steady voltage indicating that the current was at least moderately steady.

(2) With atmospheric pressure in the tube the potential was limited to 500,000 volts by brush discharge in the air outside the tube. This indicates that the former limitation to 300,000 volts was not due to current down the wall of the tube.

(3) Increasing the pressure from 4×10^{-6} mm to 4×10^{-4} mm by the admission of hydrogen did not reduce the voltage below that attainable at the lower pressure. This shows that the discharge is not maintained by the free gas in the volume of the tube.

(4) A solder electrode in place of nickel resulted in a much lower equilibrium voltage as well as a somewhat higher gas pressure. Evidently the voltage is dependent on the nature of the electrode surface.

(5) During outgassing of the electrodes by the discharge the voltage across the tube gradually increased. This indicates that the gas content of the electrode is a factor, as might be anticipated from the fact that solder with its high gas content reduced the voltage.

The experimental evidence given above indicates that the discharge within the tube is due to ionization at the electrode surfaces because of impacts of ions, electrons, and photons. To illustrate this mechanism of breakdown, let us suppose that, on the average, an electron impinging on the anode liberates there A positive ions and B photons which reach the cathode, and furthermore that a positive ion impinging on the cathode liberates there C electrons which pass to the anode, while a photon impinging on the cathode liberates D electrons which pass to the anode. Then evidently the condition for a discharge is that $AC+BD>1$. It seems that this mechanism would explain the initiation of discharge not only in the present experiment but also in certain experiments of others in the past. In many such cases it has been difficult to account for the onset of discharge.

A breakdown by this mechanism can be eliminated by screening the electrodes with grids at such potentials as to trap secondaries produced on these electrodes. The secondaries ejected from the grid will be smaller in number not only by the ratio of projected grid area to plate area, but also because of the fact that the grid may be constructed of such a material as tungsten and may be thoroughly outgassed. The condition for the initiation of discharge then becomes $S_g/S_p \cdot(ac+bd)>1$ where a, c, b, d are the coefficients for the outgassed grids, and S_g and S_p are the areas of grid and plate respectively.

We take pleasure in expressing our thanks to Princeton University where, in the Palmer Physical Laboratory, this work was carried out.

Ionization and Scattering Accompanying Positive Ion Impact in Gases*

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(Received November 19, 1932)

The ionization produced by K^+ ion impact in A, Ne, He, N_2, CO, H_2, and Hg was studied for voltages ranging from 0 to 4000 volts. These results check with the results of previous investigators wherever it was possible to make comparisons. The A curve saturates (i.e., the ionization in A approaches a constant maximum value as the voltage is increased) at 4000 volts. The Ne curve shows a tendency to saturate at 4000 volts. The ionization in He and H_2 was very weak. N_2 and CO ionize equally well and their curves fall just a little above the neon curve. The minimum potentials at which ionization sets in vary from 100 volts for A to 1600 for H_2. Accurate measurement of these potentials was not attempted. It is shown that when the results are plotted against the kinetic energy of the impinging ion-molecule system (relative to its center of mass) that the various ionization potentials show a comparatively small range. The scattering experiments show that at low voltage a few of the K^+ ions make direct impact in mercury and are reflected with 4/9 of their original energy which is the value expected from conservation of momentum and energy. Small angle scattering was also observed in this case and for K^+ and Na^+ in argon. No ions are here observed with appreciable velocity in the reverse direction. The evidence indicates that the gases which ionize most readily are also most effective as a scattering agent. It is suggested that ionizing collisions are glancing collisions.

1. INTRODUCTION

THE ionization of noble gases by the impact of the various alkali ions has been investigated for acceleration voltages up to 750 volts.[1] The purpose of this investigation was first to extend the ionization measurements to higher potentials and to include a greater number of gases, and second to investigate the nature of a non-ionizing collision.

Part I of this paper will deal with the ionization of argon, neon, helium, hydrogen, nitrogen, carbon monoxide and mercury by potassium ion impact. Part II will deal with the scattering of K^+ and Na^+ ions in mercury vapor and argon.

2. APPARATUS AND METHOD

The experimental tube is shown in Fig. 1. It resembles that of Sutton[1] except for the following modifications: (1) a system of differential pumping was employed; (2) an earthed wire gauge was placed around the filament chamber; (3) a Faraday cylinder was used to

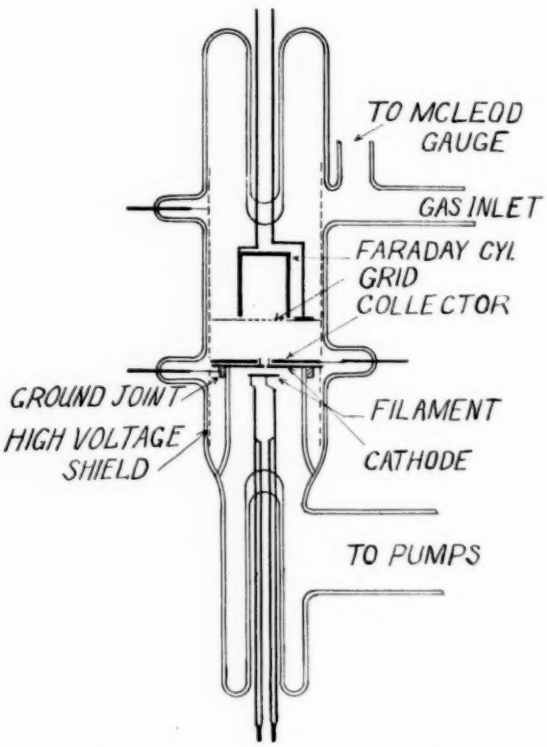

FIG. 1. Diagram of experimental tube.

* Presented at Washington Meeting, American Physical Society, April, 1932.

[1] Sutton, Phys. Rev. **33**, 363 (1929); Beeck, Ann. d. Physik **6**, 8, 1001 (1930); Sutton and Mouzon, Phys. Rev. **35**, 694 (1930); Beeck and Mouzon, Ann. d. Physik **11**, 858 (1931); Ann. d. Physik **11**, 737 (1931); Zwicky, Proc. Nat. Acad. **18**, 314 (1932). Mouzon has published a paper (Phys. Rev. **41**, 605 (1932)) in which he extends the voltage to 2000 volts, since this paper was prepared for publication.

catch the primary ion beam. It was imperative that the filament chamber be evacuated to such an extent that the residual gas would not support a discharge at the high voltages used. Thus it was necessary to employ a system of differential pumping. High-speed mercury vapor pumps were used and a 1000-fold pressure difference could be maintained across the cathode with 0.01 mm pressure in the ionization chamber. A Faraday cylinder covered with a wide mesh grid was employed to catch the primary ion beam and to reduce the effect of the secondary electron emission to a minimum.

The tube is divided into two compartments by the cathode. One compartment contains the filament and the other the electrodes used for the ionization measurements. The cathode was fitted to the re-entrant glass tube containing the filament by a closely fitting, dry, ground joint. The positive ions were liberated from a closely wound, tungsten spiral filament coated with Kunsman[2] catalyst. These ions were then accelerated to the iron cathode and in part projected into the upper chamber through a 0.5 mm hole in the cathode. This chamber contained gas at pressures which were varied from 0.03 mm to 0.09 mm for various runs. Here the ionizing collisions were made. The electrons formed by ionization were drawn to the collector which was placed immediately over the cathode. The collector was protected from the incident ion beam by a small projection or "snout" integral with the cathode.

The grid served to bound the region for which ionization was measured and the distance between it and the collector was 2 cm. This grid was made of 1 mil tungsten wire and the spacings were about 2 mm. Thus very little area of metal was exposed to the positive ion beam.

The main tube voltage was supplied by a bank of four d.c. motor generators connected in series. The voltage applied to the tube could be varied continuously from 0 to 4000 volts by a high-resistance potentiometer.

The gas technique varied for the different gases used. The hydrogen, nitrogen and carbon monoxide gases were manufactured as they were used, and admitted into the ionization chamber by a fine capillary of suitable size; the gas which diffused through the cathode was pumped out into the room. The noble gases were admitted into the system after it had been pumped out and shut off from the fore pump. Instead of pumping these gases out into the room they were shunted back into the ionization chamber so that the same gas was used over and over.

The hydrogen was prepared by the electrolysis of phosphoric acid and the nitrogen and carbon monoxide were prepared according to a method described by Warren.[3]

Since these gases (H_2, N_2 and CO) were supposedly prepared in a pure state no method of purification was attempted. The noble gases were purified by either a misch-metal glow discharge or charcoal tube placed in the circulatory system between the two-stage diffusion pump and the ionization chamber. The results in helium and hydrogen were found to be extremely sensitive to traces of impurity as has been reported by Sutton[1] (for helium).

Mercury vapor was admitted into the tube from a bulb sealed to the side of the tube at the point marked "gas inlet" in Fig. 1. The bulb containing the mercury was placed in a heated oil bath to give the desired temperature, while the tube as a whole was slightly superheated to prevent condensation. The tube was protected from water and grease vapor by liquid air traps. The glass line to the McLeod gauge, which passed through liquid air was about 1 meter in length (10 mm tubing) and a constriction was added near the tube so that Hg pressure in the tube was very nearly equal to that in the Hg bulb.

A diagram of the electrical circuit is shown in Fig. 2. Both the collector current and primary current were measured on a galvanometer G_1 which had a sensitivity of 10^{-11} amp./scale div. This was made possible by a highly insulated 4-pole double-throw switch. Galvanometer G_2 (sensitivity of 4×10^{-11} amp./scale div.) was connected in the primary circuit at all times and used to check the steadiness of the primary current.

The grid was made negative with respect to the collector so that the ionization electrons

[2] Kunsman, Rev. Sci. Inst. **1**, 654 (1930).

[3] Warren, Phil. Mag. **42**, 246 (1921).

formed between the grid and the collector would go to the collector. This potential difference did not exceed the electron ionization potential of the gas. The secondary electron emission from the walls of the Faraday cylinder reaching the collector was reduced to a minimum when the Faraday cylinder was made six or seven volts positive with respect to the grid. Below 1000 volts accelerating potential the secondary electron current to the collector (with $<10^{-5}$ pressure in tube) was less than 1 percent of the primary ion current, at 4000 volts this increased to about 4 percent. This secondary electron current was undoubtedly due to emission from the grid. In all cases except for argon (where the correction

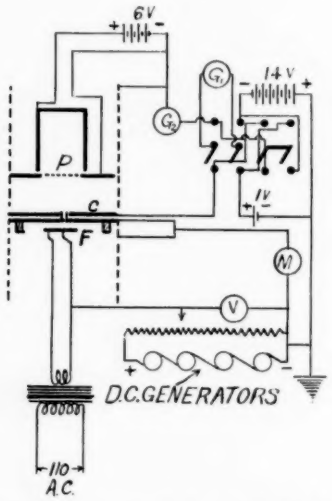

FIG. 2. Diagram of electrical circuit.

was only slight) the ionization curves were corrected for this secondary emission.

The number of ions returning to the cathode snout had to be investigated before any degree of confidence could be placed in the results. The collector current and primary current were studied as a function of the voltage for various gas pressures. It was discovered that the snout played a rather important rôle when the gas pressures were high enough to stop an appreciable number of positive ions close to it. This was not very important, however, for the pressures used in this experiment. The collector was made 1 volt positive with respect to the cathode so that any electrons formed near the snout would be drawn to the collector.

3. Experimental Results and Discussion

Part I. Ionization in A, He, H_2, N_2, CO and Hg

(*a*) *Experimental curves on ionization.* The experimental curves showing the number of ions formed per ion, per cm path, at 1 mm gas pressure, by K^+ ion impact as a function of the tube voltage are shown in Fig. 3.

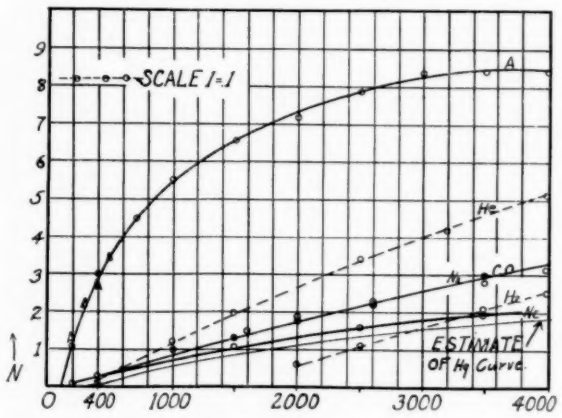

FIG. 3. Number of ionization electrons formed per K^+ ion per cm path through gas at 1 mm pressure as a function of the K^+ ion energy in volts. The ordinate scale for H_2 and He is to be reduced by a factor of ten.

These curves are each the result of the averaging of several runs. In test runs the gas pressure was varied from 0.03 mm to 0.09 mm yet for A, Ne, N_2 and CO the different series of observations checked (when reduced to same standard pressure of 1 mm) within 10 or 15

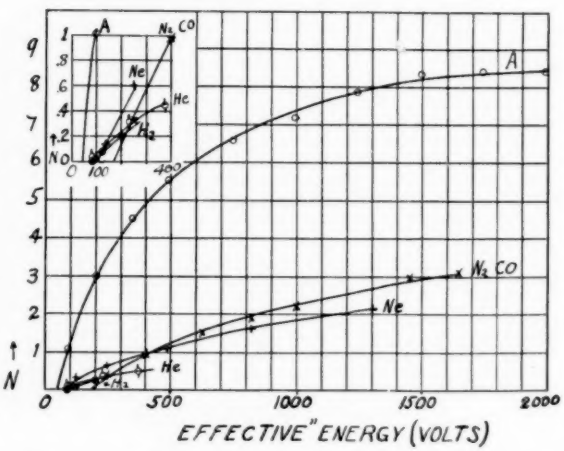

FIG. 4. Number of ionization electrons formed per K^+ ion per cm path through gas at 1 mm pressure as a function of the "effective" energy ($MV/M+m$ where V is the voltage of Fig. 3) of the K^+ ion.

percent (which is as close as the McLeod gauge can be read with certainty). This shows that the observed effect was proportional to the gas pressure. However, final data were taken in the pressure range of 0.03 mm to 0.05 mm. The results for A agree well with those of Beeck whose results are indicated by the triangles on the curve; Sutton's values are somewhat higher. The precision in the case of helium and especially hydrogen is somewhat less than this since the effect is very small and the question of gas purity is important. The ionization efficiency of mercury has also been computed (from Fig. 5). The presence of reflected ions introduces a complexity here and the results are subject to a rather larger error than for other cases.

The ionization in argon is remarkably higher than in the other gases. The argon curve saturates at about 4000 volts while the other curves (except for neon) show only a very slight bending. The neon curve shows some sign of approaching saturation.

From the results of Beeck and Mouzon,[4] which are limited to the noble gases, one should expect the degree of ionization to go up with the mass of the target particle until the masses are equal. If this relation between mass and ionization efficiency holds for all gases, one would expect hydrogen to be the lowest, and it is the lowest. The curves for N_2 and CO come in just above neon which seems to be about the place one would expect to find them, if one uses the mass of the molecule rather than that of the atom.

Not much can be said concerning the expected variation of ionization with mass of target particle when the mass of the target particle exceeds the mass of the impinging particle. It is seen that the curve showing ionization in mercury (a very massive atom) is among the lowest in Fig. 3.

The maximum ionization efficiency for K^+ ion impact in argon and neon is of the same order of magnitude as that found for ionization by electron impact. In argon the number of ions formed by electrons per cm path length at 1 mm gas pressure is about 10.3 at 150 volts[5] (the voltage of maximum efficiency) at 4000 volts which is approximately the voltage of maximum efficiency for K^+ ions the corresponding number of ions formed by a K^+ ion is 8.5. In neon the number formed by electrons is about 3.2 as compared to 2.1 for K^+ ions. The neon curve has not, however, reached its maximum at 4000 volts. The curves for the other gases do not lend themselves to such a comparison since they have not yet reached their maxima.[6]

The minimum potentials which were found to be necessary for ionization range from about 100 volts for argon, to about 1600 for hydrogen. These values agree quite well with the earlier results of Beeck, although in a later paper he gives a considerably higher value for neon.[7]

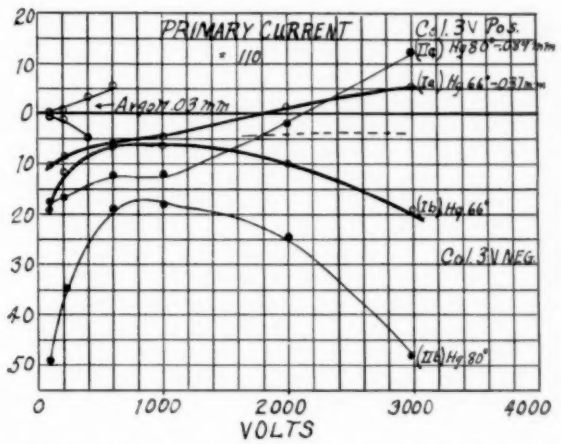

FIG. 5. Collector current as a function of the main tube voltage when the grid is made ±3 volts with respect to the collector. Curves I(a) and I(b) are for 0.37 mm Hg pressure and II(a) and II(b) are for 0.089 mm. Similar curves for argon are included for comparison. These curves show reflections of positive ions by Hg vapor at the lower tube voltage. The dotted line represents the assumed reflected current at high voltage.

Previous investigators have failed to detect ionization in hydrogen—in most cases because the voltages used were too low. Gurney[8] used potentials as high as 7000 volts but was forced to work with low pressures and low primary

[4] Beeck and Mouzon, Ann. d. Physik **11**, 737 (1931).

[5] Compton and Van Voorhis, Phys. Rev. **26**, 436 (1925).

[6] Compton and Van Voorhis, reference 5, values of maximum efficiencies for electron ionization are as follows: Hg, 19.5; A, 10.3; N_2, 10; H_2, 3.5; Ne, 3.1; He, 1.75.

[7] Beeck, reference 4. (Some of the later results of Beeck differ considerably from his earlier results. In view of the fact that no specific explanation of this lack of agreement is given in his later paper one is inclined to compare with the most favorable results.

[8] Gurney, Phys. Rev. **32**, 795 (1928).

currents. This fact may perhaps account for the uncertainty of his results.

(*b*) *Ionization as function of energy available for ionization.* When two particles of comparable masses collide, only a portion of the kinetic energy can be lost in the impact. If one of the particles (mass M) is at rest and the other moving with kinetic energy $\frac{1}{2}mv^2$, the maximum energy which may be lost is $\frac{1}{2}[mM/(M+m)]v^2$. In Fig. 4 the observed ionization currents are plotted against this available energy. One no longer observes the large differences of ionization potentials. Except for N_2 and CO the "reduced" ionization potentials are all less than 100 volts. Even on the reduced scale there is no correlation of ionization potentials with ionization potentials for electron impact.

Part II. Scattering of alkali ions by gases

(*a*) *K^+ ions in mercury at low vapor pressure.* When K^+ ions strike atoms of mercury vapor at voltages too low to permit ionization some of the ions are reflected backward from the heavier atoms and give a positive current to the collector. This offers a means of studying the nature of the collision between ion and atom.[9]

The K^+ ions were projected into the Hg vapor as described for the other gases mentioned above. Fig. 5 represents the current to the collector as a function of the tube voltage. In these curves the potential difference between the grid and collector was 3 volts. In I(a) and II(a) the field was in such a direction as to attract positive ions to the grid and send electrons to the collector. In curves I(b) and II(b) this field was reversed so that the grid attracted electrons and repelled positive ions to the collector.

These curves of Fig. 5 show a current to the collector at low tube potentials which is due to the reflection of ions on impact; this has not been observed in any of the other gases. At higher tube voltage the characteristic ionization is shown (evidenced by the separation of curves I(a) and I(b)). In curves I(a) the collector collects positive ions at low voltage and this in spite of the 3 volt *retarding* potential. This must be due to reflection of K^+ ions by the mercury molecules. The curve deflects upward at 600 volts, due to ionization setting in, and crosses the axis when this ionization current becomes greater than the reflected ion current. In curve I(b) this 3 volt field is reversed, now *attracting* positive ions to the collector instead of *repelling* them. Slow speed ions are attracted to the collector and electrons are repelled to the grid. Thus curve I(a) is a measure of the high-speed reflected positive ions plus slow speed *negative* ions (electrons—products of ionization) and curve II(b) is the sum of the high-speed positive ions plus slow-speed *positive* ions. The separation of the curves I(a) and I(b) at low voltage is due to slow K^+ ions which have either lost most of their energy by second collisions or to those which approach the collector so obliquely as to have but a small component velocity normal to it. The number of these "small velocity component" ions naturally decrease with increasing voltage. Above 900 volts the slow speed ions are largely due to ionization.

The curves I(a) and I(b) were taken with the mercury at 66°C (pressure of 0.037 mm). They show a reflection of about 15 percent at 100 volts. According to the simple kinetic theory the mean free path (mercury in mercury) at this pressure would be 0.37 mm. The dimensions of the apparatus were such that only those ions making collisions angles greater than approximately 130° would reach the collector. Since this angle is about one-fourth of the total solid angle and if all angles of scattering were equally probable the whole scattered current would be about sixty percent. This corresponds to an experimental mean free path of about 4 cm.[10] This is, obviously, very much larger than the kinetic theory value and it is quite probable that these high-speed ions scatter through smaller angles. These curves show that the m.f.p. is decreasing as the velocity is lowered. At higher voltage the scattering decreases to 5 percent (at 800 volts) and the separation between the curves (corresponding to reflected ions with small velocity) decreases.

[9] Cox, (Phys. Rev. **34**, 1426 (1929)) and Thompson, (Phys. Rev. **35**, 1196 (1930)) have studied the motion of slow Li^+ and Cs^+ ions in Hg, H_2 and He.

[10] Durbin, Phys. Rev. **30**, 844 (1927), has measured the m.f.p. for K^+ ions having velocities corresponding to 0 to 250 volts in several gases but not in Hg. This value is, however, very much larger than his value.

Above 800 volts the reflection is partly masked by the ionization current. The reflection accounts in part for the dissymmetry in the positive and negative currents. The number of reflected ions probably stays nearly constant or perhaps decreases somewhat at higher voltage as shown by the hypothetical (dotted) line.

From other experiments it was found that ionization sets in at about 300 volts. It does not become an important factor for several hundred volts further, as is seen by the fact that curves I(a) and I(b) do not diverge below 600 volts. If the "hypothetical" reflected current (shown by dotted line) is approximately correct, the positive ion current is almost twice as large as the negative current at 3000 volts. Such a dissymmetry is to be expected. The Faraday cylinder was always positive with respect to the grid (to eliminate the effect of secondary electrons). Hence, all negative ions produced between grid and cylinder are drawn to the cylinder. Curve I(a) is a measure only of the ions formed between the grid and collector. Curve I(b) on the other hand, measures also the positive ions forced out of the cylinder. In other words, curve I(b) is a measure of the ions formed for a path about twice as long as the path for curve I(a).

It is not possible to estimate this ionization current with the precision of the other ionization curves but taking the negative current as equal to 10 divisions (at 3000 volts) one obtains about 1.4 for the number of ions formed per cm path at 1 mm mercury vapor pressure.

Curves II(a) and II(b) were taken with a higher vapor pressure in the tube. The pressure has been something more than doubled and one observes a little more than twice the ionization and something more than twice the reflected current and a great many more slow-speed reflected ions. (The separation between the curves has increased.) This large increase in slow-speed reflected ions is due to multiple collisions since the chance of two collisions is quadrupled as the pressure is doubled.

Curves similar to these are shown for argon for a small range of voltage at a pressure nearly equal to that for I(a) and I(b). The same dissymmetry is shown but there is no evidence at any voltage of reflected ions. Ionization begins at 100 volts.

(*b*) *"Directed energies" of reflected ions.* The argon molecules are equal in mass to the K^+ ions and direct reflection of K^+ ions from argon is not to be expected. In a direct impact the energy is handed over from the K^+ to the argon molecule. The energy retained after an elastic collision at any angle is, of course, derivable from the simplest application of conservation of energy and momentum.[11] One may reasonably assume that the collisions of K^+ ions in mercury at low voltage are elastic. Limiting the consideration to "head on" collisions the K^+ ion should be reflected back with about 2/3 of its original velocity, i.e., 4/9 of its original kinetic energy.

The energy distributions curves for 50, 100 and 200 volt K^+ ions impinging in Hg vapor are shown in Fig. 6. Here the potential difference between grid and collector (which was held constant in Fig. 5) was varied and these curves of Fig. 6 are obtained by plotting the collector current as a function of the difference of potential. To the left of the zero ordinate axis the curve represents positive ions moving forward, to the right it represents positive ions reflected backwards. The abscissas give the stopping (or accelerating potential between grid and collector. The ability to overcome a stopping potential depends not upon the total kinetic energy of the ion, but upon what one may call the "directed kinetic energy." By this is meant $\frac{1}{2}mv_x^2$ when v_x is the component of velocity in the direction of the field. It is this directed kinetic energy which is given (in terms of electron volts) by the abscissas.

Curves A and B were taken for different pressures, as indicated in the figure. In each case two sets of curves are shown. The one set with the solid circles represents the energy distribution of the K^+ ions in a vacuum. The hollow circles represent the energy distribution with Hg vapor in the tube at 74°C and 58°C.

In the case of the vacuum curves the positive ions are seen to have a rather small range of velocities. A current is received by the collector when the retarding potential on the grid (*col.*

[11] Joos and Kulenkampf, Phys. Zeits. **25**, 257 (1924).

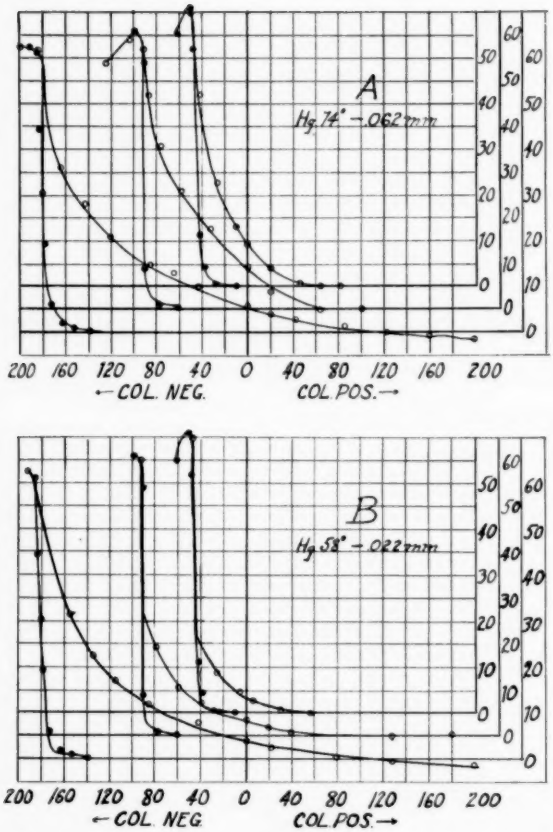

FIG. 6. Collector current as a function of the potential difference between grid and collector for 50, 100 and 200 volt K^+ ions projected into Hg vapor. Solid points represent results with vacuum in tube. These curves give substantially the "normal component" of the energy distribution among the positive K^+ ions after impact.

neg.) is almost as great as the tube voltage,[12] which is to be expected. When the Hg vapor was in the tube the total ion current is 60 divisions as in the vacuum case, but now the current is received with *smaller* or even *reversed* voltages on the grid.

When the grid is made negative so that the field repels ions from the collector the current decreases and reaches zero at about 45 volts (for 50 volt ions). This 45 volts gives a measure, presumably, of the fastest *reflected* ions. This is in general agreement with expectations. If it be assumed that the collision takes place in the neighborhood of the grid the ions involved will have an energy of 100 volts at this point on impact. (The field which is indicated as (*col. pos.*) was applied by making the grid more negative with respect to filament and snout rather than by changing the potential of the collector). According to the theory, an ion making a direct collision should be reflected back with 4/9 of this energy, i.e., be able to overcome a retarding potential of about 40 volts which is made nearer to the collector than this, a larger stopping potential on the collector should be applied. However, there are other factors (multiple collisions, etc.) which are very important and all of which tend to operate in the opposite direction.

In general, if V is the cathode potential (with respect to the filament) and R the grid potential, the energy of the ion as it reaches the grid is $V+R$; after direct impact it is 4/9 of this. Hence the maximum *retarding* potential is given by $(4/9)(V+R)=R$ or $R=(4/5)V$. In other words, when the potential R is equal to $(4/5)V$ the elastically reflected K^+ ions from Hg will just be prevented from reaching the collector. The 50 volt ions should be stopped by 40 volts, the 100 volt ones by 80 volts, and the 200 volt ions by 160 volts. Actually, the curves shown for 100 volt positive ions indicate only a slightly greater stopping potential than the 50 volt curve. In the case of the 200 volt ions ionization begins to play a rôle. The grid potential added to the tube voltage of these ions gives these ions at the extreme right of the curve some 400 volts which is able to produce ionization and cause the curve to cross the axis. This makes the interpretation difficult but it is clear that the stopping potential is not less than 120 volts. In view of the neglected factors these results may be considered as in rather good agreement with the theory.

Collisions of a more glancing type are certainly quite prominent. This can be seen from the difference between the vacuum curves and the Hg curves to the left of the zero axis of ordinates. It is clear that for a mercury pressure of 0.062 mm there are practically no ions which entirely miss making mercury collisions in any of these curves. In each case the vapor curve starts to break away from the vacuum curve rather quickly. There seem to be a great many ions

[12] As the retarding voltage is made still larger the collector current drops off slightly because the ion beam is turned back sooner and more of it reaches the snout and less to the collector.

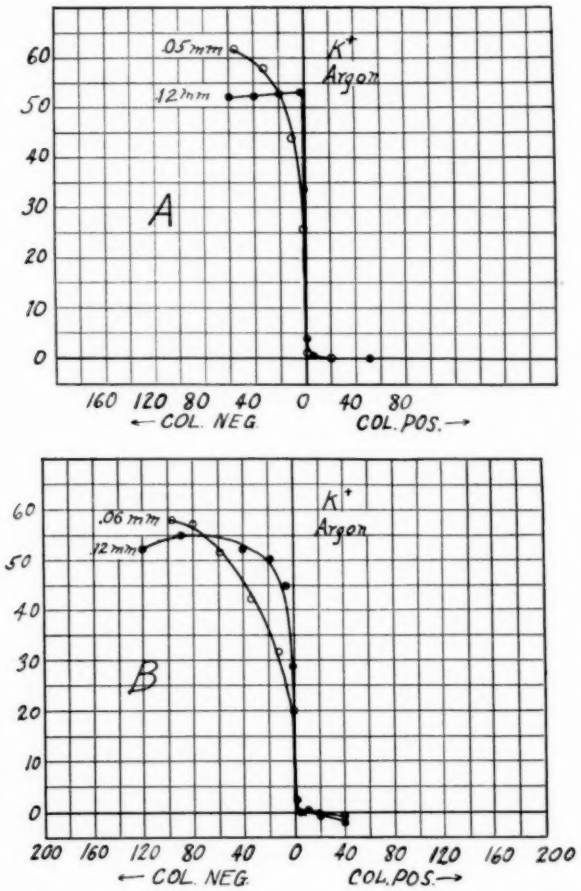

FIG. 7. Collector current as a function of the potential difference between grid and collector for 50 and 100 volt K^+ ions projected into argon. Similar to curves of Fig. 6 for Hg.

which have retained 50 or 75 percent of their original energy (i.e., stopped by a retarding voltage on the grid of 50 to 75 percent of the tube voltage) but very few indeed with the full energy. Fig. 6B shows similar curves for much lower vapor pressure. The maximum reflected velocities (the intercept "*col. pos.*") are about the same as before.

The curves for 50 volt and 100 volt ions quite clearly intersect the vacuum curves (Fig. 6B) showing that in these cases something like 50 percent of the ions suffer no energy losses. In case of the 100 volt curve the number which have escaped collision seems rather higher than for the 50 volt curve; for the 200 volt curve all of the ions seem to have lost energy. It is not clear whether small energy losses are indeed more probable with higher velocity particles or whether the difference is due to some experimental difficulty. This point would deserve further investigation.

(*c*) *K^+ ions in argon.* Curves showing the velocity distribution for 50 and 100 volt K^+ ions projected into argon are shown in Figs. (7A and B) respectively. In general, the argon curves are of an altogether different type from the mercury curves. They indicate that the mean free path of K^+ ions in argon is shorter than in mercury. At 0.12 mm pressure multiple collisions produce complete energy losses. The curves show that K^+ ions are not reflected backward by the argon atoms; no such reflection can occur because the K^+ ions and argon atoms are of equal mass.

(*d*) *Na^+ in argon.* A distribution curve for 100 volt Na^+ ions in argon is shown in Fig. 8.[13] The reflected current (if it existed at all) is very small as is evidenced by the fact that the curve goes to zero very soon on the right side of the zero axis of ordinates. This is to be

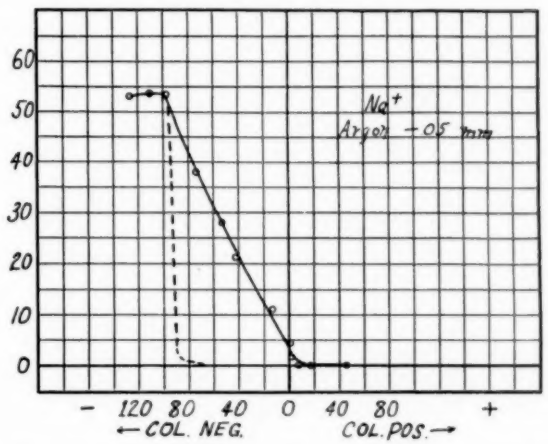

FIG. 8. Curve for Na^+ ions impinging in argon, similar to Figs. 6 and 7 for K^+ ions in Hg and argon. The dotted line shows the assumed distribution of the energy of the Na^+ ions in a vacuum.

expected from a consideration of the relative masses of sodium and argon. Na^+ reflects from Hg much the same way as K^+, but a detailed study of this was not made.

(*e*) *Probable nature of ionizing collisions.* One last observation in this study of the nature of ionic impact should be recorded. It pertains to

[13] The dotted curve represents the assumed distribution curve for Na^+ in a vacuum.

the ionizing collision. The secondary electrons and positive ions resulting from ionization are collected by a small potential difference. I(a) and (b) of Fig. 5 were taken with a collector voltage of ± 3 volts. A larger voltage adds little to the separation of the curves. This would seem to indicate that the Hg ion is propelled forward at the moment of formation with negligible speed. This means that the collisions which produce ionization are of a "glancing" type, the K^+ ion suffering little change in momentum. If this interpretation is correct, it is, to say the least, a remarkable state of affairs. It does not agree with Zwicky's[1] fundamental hypothesis that the probability of ionization depends on the momentum transfer.

The author takes this opportunity to express his appreciation of the advice and suggestions given by Professor J. A. Eldridge under whose direction this work was done.

Momentum Transfer to Cathode Surfaces by Impinging Positive Ions in a Helium Arc

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(Received November 18, 1932)

The momentum transfer to an auxiliary cathode has been studied in the positive column of a low-voltage helium arc. The auxiliary cathode was a flat molybdenum plate insulated on one side by glass and suspended in such a way that its deflection gave a measure of the pressure against it. The measured pressure on the cathode is believed to be due to two phenomena. The first is the recoil of those ions which retain some of their kinetic energy after neutralization. The second is a radiometer effect due to the heating of the cathode by positive ion bombardment. On the basis of these assumptions it was possible to calculate from the experimental data an accommodation coefficient for helium positive ions and the fraction of the measured current carried by electrons. Although the accuracy of the experiment is not high, the values of the accommodation coefficient are in qualitative agreement with those obtained by Compton and Van Voorhis. The fraction of the current carried by electrons agrees fairly well with the results of Harrington.

INTRODUCTION

IN 1929 Tanberg[1] measured the pressure on the cathode of a copper arc in vacuum. On the assumption that this pressure was the recoil resulting from the evaporation of copper atoms, it was possible to compute a temperature of about 500,000 degrees for the cathode spot. Compton[2] showed that if one assumed a reasonably small departure from unity in the accommodation coefficient for the positive ions such that they retained after neutralization a small fraction of the kinetic energy gained in the cathode drop, one could account for the observed pressure. Although the impact of a charged ion against the cathode contributes nothing to the pressure against it (on account of the counterbalancing pull during its attraction to the cathode), nevertheless if the neutralized ion leaves the cathode with any momentum there is imparted to the cathode an equal opposite momentum. Evidence for the existence of an accommodation coefficient for positive ions was found by Compton and Van Voorhis[3] from measurements of the heating of an auxiliary cathode by positive ion bombardment in a low-voltage arc.

At the suggestion of Dr. Compton, the work reported here was undertaken to test the above hypothesis with a nonvolatilizing cathode and to look for further evidence for the existence of an accommodation coefficient for positive ions. With a nonvolatilizing cathode, there is no possibility of a pressure as a result of a stream of metal vapor leaving the cathode. Preliminary work along this line, carried on at Princeton University, was reported in a letter to the Editor.[4] As a result of this preliminary experience, the apparatus has been redesigned and the work carried through, during the past year, to much more reliable conclusions, which are here reported.

The accommodation coefficient was originally introduced and defined by Knudsen[5] in terms of temperatures by $\alpha=(T_i-T_r)/(T_i-T_s)$, where T_i, T_r and T_s are the temperatures of the incident gas molecules, the reflected molecules and the reflecting surface, respectively. Langmuir and Blodgett[6] redefined the coefficient in the more general terms of energies, thus avoiding restrictions as to Maxwellian distribution of velocities among the gas molecules. In the present paper,

[1] Tanberg, Phys. Rev. **35**, 293 (1930); Phys. Rev. **35**, 1080 (1930).

[2] K. T. Compton, Phys. Rev. **36**, 706 (1930).

[3] C. C. Van Voorhis and K. T. Compton, Phys. Rev. **35**, 1438 (1930); Phys. Rev. **37**, 1596 (1931).

[4] Lamar, Phys. Rev. **37**, 842 (1931).

[5] Knudsen, Ann. d. Physik **34**, 593 (1911).

[6] Blodgett and Langmuir, Phys. Rev. **40**, 78 (1932).

this more general definition is used and the very high energy of the molecules in comparison with the average energy of the surface atoms makes the latter term so insignificant as to justify its neglect.

Ideally Simple Theory

Imagine a plane collecting electrode immersed in a uniformly ionized gas and maintained at a potential V negative with respect to the surrounding space. If its current density I consists entirely of the positive ions which are drawn into it through the surrounding space charge sheath, the pressure P against it is due to the rebound of these ions following their neutralization at its surface. This rebound energy V_r, in electron-volts, is expressible in terms of the accommodation coefficient $\alpha=(V-V_r)/V$. Under these conditions the pressure is

$$P=(I_+/e)(2MeV_r)^{1/2}=(I_+/e)(2MeV(1-\alpha))^{1/2}.$$

Here the rebound is assumed to be normal to the surface. If, as is more probable, the rebounding neutralized ions are scattered in random directions, a factor 2 should appear in the denominator. This comes about in the integration of the component of the momentum normal to the collector surface. The integration is carried out over a hemisphere cut by the plane of the collector surface from a sphere whose center lies in an element dS of the collector surface. In the apparatus to be described, the plane collector was the bob of a pendulum, whose deflection gave a direct measure of the pressure against the collector.

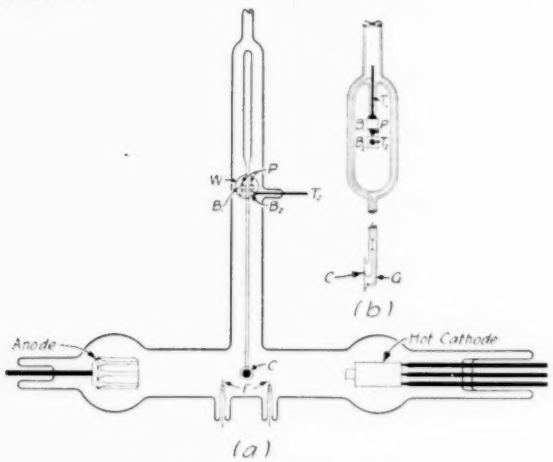

Fig. 1. Diagram of arc tube.

Actually the experiment was not so simple, because of the existence of three complicating factors: (1) lack of homogeneity of ionization, so that the conditions around the collector changed as the pendulum deflected; (2) radiometric force due to heating of the collector surface by the energy there liberated; (3) presence of secondary electrons emitted from the collector and contributing appreciably to its current. These complications are taken into account in the actual conduct of the experiment and analysis of results.

Apparatus

A diagram of the arc tube is shown in Fig. 1. The arc cathode which is of the thermionic type and the arc anode were obtained from the General Electric Company. A detailed sketch of the auxiliary cathode C is shown in Fig. 1b. It consists of a molybdenum plate insulated on one side by the glass G. A small clearance was left between the glass and the plate to prevent any sputtered metallic films deposited on the glass from making electrical contact with the auxiliary cathode. The auxiliary cathode assembly was part of a glass pendulum suspended in a side tube as shown. In order to support the pendulum a tungsten rod T_1 was sealed through the glass of the pendulum. A steel block B_1 was attached to the rod T_1 by means of a set screw. To the block were fastened two steel points P. These points set in polished indentations in the steel block B_2 which was supported by a tungsten rod T_2 sealed through the glass of the arc side tube. The current carrying leading-in wire from the auxiliary cathode C went up the inside of the hollow glass pendulum and was attached, on the inside, to the tungsten rod T_1. In order to prevent the carrying of current by the sharp steel points, a two mil copper wire was shunted between the two steel blocks B_1 and B_2. Metallic contact could then be made from the outside of the arc tube to the auxiliary cathode C by making connection with the tungsten rod T_2.

A small mirror (not shown in the figure) was fastened to the steel block B_1. A light beam was introduced through the lens-shaped window W on to the mirror and focussed on a scale 1.5 meters away. A perfect vacuum joint was made

between the lens and the ground surface of its supporting side tube by means of Glyptal lacquer.

A small cylindrical probe wire (not shown in the figure) was sealed through the main arc tube immediately behind the auxiliary cathode *C*. On each side of the auxiliary cathode are the two test filaments.

The thermionic equipotential cathode was heated by alternating current from a transformer. A steady e.m.f. for the arc was supplied by a 120 volt bank of storage batteries. The resistance in series with the arc was placed on the hot cathode side of the batteries, so that it was possible to obtain, from a potential divider across the main batteries, 120 volts negative with respect to the anode for application to the auxiliary cathode. An additional 200 volts for the auxiliary cathode were obtainable from storage B batteries. The voltage of the auxiliary cathode was controlled chiefly by a high series resistance so as to eliminate all possibility of striking an arc to this cathode.

The helium was introduced into a two-liter glass reservoir bulb through a chabizite trap immersed in liquid air. The trap had previously been baked out at 500°C. In the reservoir bulb was an iron anode and a misch-metal cathode between which an arc was maintained for further purification of the helium.

The pendulum was set up and calibrated dynamically before the tube was assembled. The necessary data were the weight of the pendulum, its period for small oscillations and its period with an additional known load at a known distance from the axis of oscillation. From these, the distance of the center of gravity from the axis and thus its sensitivity could be easily calculated. It was feared that the current carrying leading-in wire might introduce an additional torque; so after the tube had been assembled, the period of the pendulum was again measured. As its value was within a percent of the previously determined value, it was evident that the leading-in wire introduced no appreciable torque.

After filling the tube to the desired pressure of helium and allowing the hot cathode to reach its normal temperature, the arc was started by means of a high-frequency leak tester.

Experimental Procedure and Calculation of Results

The ideal conditions described in the simple theory above were not entirely realized in the actual discharge tube. It was found necessary, therefore, to take certain data by way of correction as follows. It was found that even with the auxiliary cathode floating (i.e., with electron and positive ion currents to it equal) the reading of the scale (and thus the pressure acting on the cathode assembly) changed as the total arc current changed. With increasing arc current, the motion of the cathode was always away from the center of the arc tube. A reasonable assumption is that this pressure on the cathode and surrounding glass was due in part to the rebound of the neutralized positive ions, and in part to a radiometric pressure resulting from heating of the cathode assembly and from radial temperature gradients in the arc. One would expect all of these effects to be approximately proportional to the arc current for the following reasons. Langmuir and Mott-Smith[7] and others have found that at least in the case of mercury the mean kinetic energies of electrons and ions are approximately independent of arc current for constant gas pressure, and that the concentrations of electrons and ions are approximately proportional to the arc current. In this work, measurements taken with the probe electrode immediately behind the auxiliary cathode showed that the electron mean kinetic energy was approximately independent of arc current. Further test of the above assumptions was not so conclusive due possibly to the shielding action of the auxiliary cathode as it assumed different positions in the arc tube. However, for the present purposes, the assumptions are considered sufficiently well justified. The pressure due to the rebounding neutralized ions should therefore be proportional to the arc current. The heating of the cathode and surrounding glass is probably due to bombardment by electrons and positive ions and thus should also be proportional to the arc current. The radial temperature gradients existing in the tube should be proportional to the power input and (since the arc voltage was

[7] Langmuir and Mott-Smith, G. E. Rev. **27**, 449, 538, 616, 762, 810 (1924).

approximately constant) proportional to the arc current. Since the cathode moved from one position in the tube to another as the pressure acting on it changed, it was necessary to find the pressure to be expected from the above causes for different positions of the cathode in the discharge tube and to subtract these pressures as a correction from the pressures observed during bombardment under voltage. This information was obtained in the following way. Readings of the scale were recorded for different arc currents and a sample plot is shown in Fig. 2a. Subtrac-

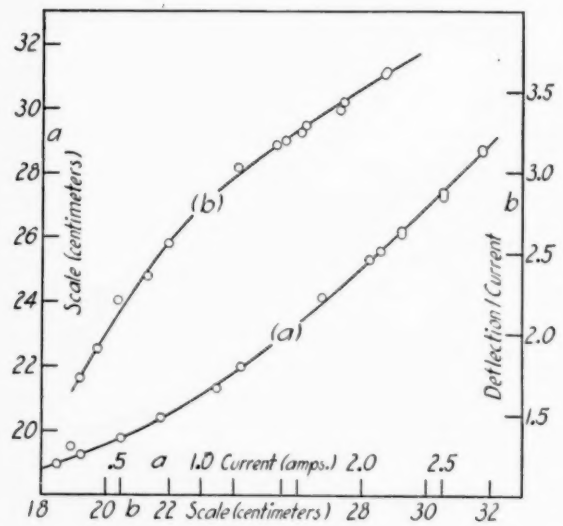

FIG. 2. Curve (a) shows scale readings as a function of arc current when the auxiliary cathode is floating. Curve (b) shows deflection per unit arc current as a function of scale reading.

tion of the reading at zero current from any other reading gave the deflection or pressure acting. Since these pressures were proportional to arc current, the ratio of pressure to arc current gave the pressure per unit arc current to be expected from the above complicating causes for the particular position of the cathode in the discharge tube. Since the scale reading gave the position of the cathode in the arc, these pressures per unit arc current were plotted against the scale reading as shown by a sample in Fig. 2b. This curve with slight alterations to be described later served as a correction curve for data taken during bombardment under voltage.

For any constant arc current the potential of the space surrounding the auxiliary cathode was determined in the following way. It was feared that the large electron currents, to be expected with the auxiliary cathode above the potential of the surrounding space, would burn out the leading-in wire shunting the supports of the pendulum. Thus the current voltage characteristic curves for the auxiliary cathode were not continued above space potential. However, current voltage curves were taken with the small cylindrical probe wire immediately behind the auxiliary cathode in the manner described by Langmuir and Mott-Smith.[7] From a plot of the logarithm of the electron current *vs.* the negative potential of the probe wire with respect to the anode, space potential was determined in the usual way. The potential difference between the probe wire and the auxiliary cathode was measured with both floating. The potential of the space surrounding the auxiliary cathode was then assumed to be the potential of the space surrounding the probe wire plus the above-mentioned difference. As the difference amounted to only a few volts, these values of space potential were considered to be sufficiently accurate for the present investigation.

In order to obtain the pressure contributed by the positive ions striking the auxiliary cathode, the deflections of the auxiliary cathode were measured for different negative voltages with the arc current constant. One hundred volts negative with respect to the anode was taken as a reference voltage (a reading of the scale at this voltage being taken after each other reading). A sample plot of deflection *vs.* negative voltage with respect to the surrounding space is shown in Fig. 3a. For convenience the scale readings are also shown. At the low-voltage end of the curve there is a kink which is attributed to that part of the radiometric pressure which results from electron heating of the auxiliary cathode. Since no electrons can reach the auxiliary cathode at the higher negative voltages, this part of the radiometric pressure should not be included in any corrections made to the curve of Fig. 3a. Thus the amount of this pressure at floating potential represented by AB was reduced to unit arc current and subtracted from the correction curve (Fig. 2b) described above at the scale reading corresponding to AB. The remainder of the curve of Fig. 2b was reduced in the same

ratio. The correction AB was taken at floating potential since it applied to the curve of Fig. 2b taken for convenience at this same potential. The deflections due to the positive ions striking the auxiliary cathode were then obtained by subtracting from each observed deflection (Fig. 3a), a correction amounting to the deflection to be expected in the absence of large negative voltage. These expected deflections were, of course, the differences in ordinates of the reduced correction curve (Fig. 2b), corresponding to the scale readings before and after voltage changes (Fig. 3a), multiplied by the arc current. The resulting curve, which presumably represents the pressures due to the positive ions striking the cathode, is shown in Fig. 4. Fig. 3b shows the measured currents to the auxiliary cathode plotted against the negative voltage with respect to the surrounding space. Use will be made of this curve later.

Since the pressure contributed by the positive ions resulted not only from their rebound after neutralization but from radiometric effects due to their heating of the cathode, a method was devised for studying this radiometric effect independently of other effects. When the auxiliary cathode was only slightly negative with respect to space an electron current was able to reach it. Such electron currents were obtained in the usual way by subtracting algebraically the extrapolated values of the apparent positive ion currents from the measured currents. Since, near space potential, these electron currents increase rapidly with decreasing negative voltages, the heating and thus the radiometric pressures due to these currents should change considerably with negligible change in the pressure due to the positive ions. The effective voltage of the incoming electrons is the sum of the mean kinetic energy and the work function of the cathode, thus the electron power input is the product of this quantity and the current. From a plot of the logarithm of the electron current *vs.* the negative potential with respect to the anode of the stationary probe wire mentioned above, the mean kinetic energy was determined in the usual way as described by Langmuir and Mott-Smith.[7] The deflections or pressures due to electron heating were corrected for other effects from a curve similar to that of Fig. 2b in the manner described above. A plot of these deflections *vs.* electron power input is shown in Fig. 5. As was expected, the deflections were proportional to electron power input. The slope of this curve which we will call $F(p)$, therefore, represents the radiometric pressure per unit power input when the gas pressure in the tube has the value p. The slopes $F(p)$ of a series of such curves are shown in Fig. 6 plotted against the pressure.

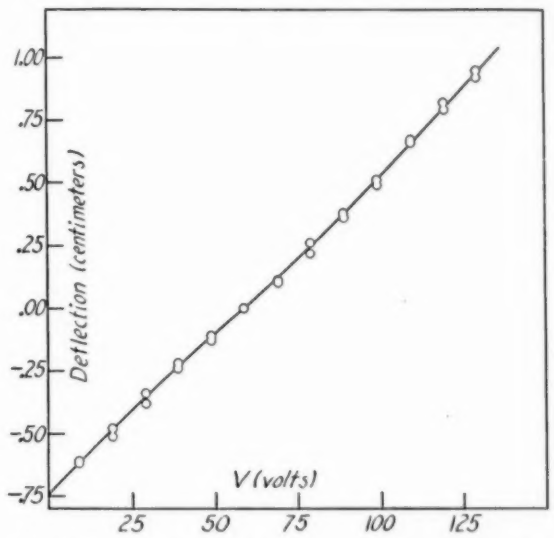

FIG. 4. Deflections resulting from bombardment of the cathode by positive ions as a function of the negative voltage of the cathode with respect to the surrounding space.

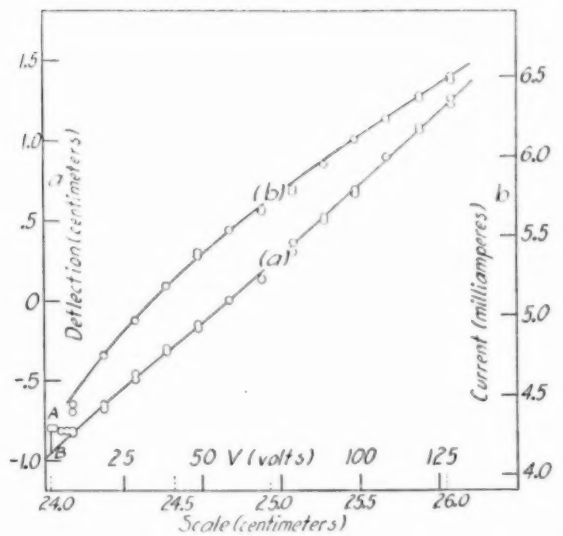

FIG. 3. Deflections and measured currents to the cathode as functions of the negative voltage of the cathode with respect to the surrounding space and of scale readings.

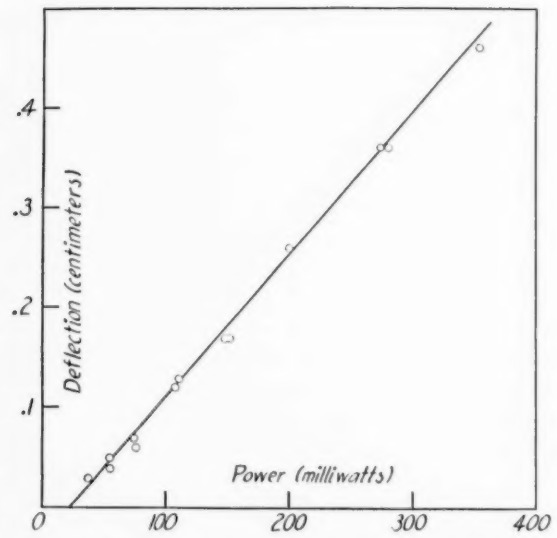

FIG. 5. Deflections resulting from bombardment of the cathode by electrons as a function of electron power input.

In order of magnitude and in shape at the higher pressures, this curve agrees surprisingly well with that given by Knudsen.[8] The deviation at the lower pressures is not surprising under the conditions of the experiment since the temperature in the arc was no doubt higher at low pressures for the same total power input.

The pressure resulting from the impact of the positive ions on the cathode can be expressed as the sum of two pressures $P=P_1+P_2$. We shall call P_1 the pressure resulting from the rebound of the positive ions after neutralization. As has been shown above,

$$P_1=(i_+/2e)(2MeV(1-\alpha))^{1/2}$$

$$=1.44(10^{-2})i_+(V(1-\alpha))^{1/2}\text{ dynes cm}^{-2},$$

where i_+ is the positive ion current density in milliamperes, V is the negative potential of the cathode with respect to the surrounding space in volts and α is the accommodation coefficient. Multiplication by the sensitivity of the pendulum, which was 2.43 cm dyne^{-1}, gives

$$P_1=3.50(10^{-2})i_+(V(1-\alpha))^{1/2},$$

where P_1 is measured in centimeters on the scale. P_2 represents the radiometric pressure resulting from heating of the auxiliary cathode by positive ion bombardment. As was shown by the use of electron heating, the radiometric force is proportional to the power input with $F(p)$ as the constant of proportionality when the gas pressure has the value p. The power input is $i_+\alpha V$ if the work function for positive ions is neglected. If it is included, V is increased by the mount φ_+ of this work function. The radiometric pressure is therefore given by $P_2=i_+\alpha VF(p)$. The total pressure P is then given by

$$P=P_1+P_2=3.50(10^{-2})i_+(V(1-\alpha))^{1/2}+i_+\alpha VF(p).$$

If f is the fraction of the measured current density i which is carried by electrons, then $i_+=i(1-f)$. By substituting, $P=i(1-f)[3.50\times(10^{-2})(V(1-\alpha))^{1/2}+F(p)\alpha V]$.

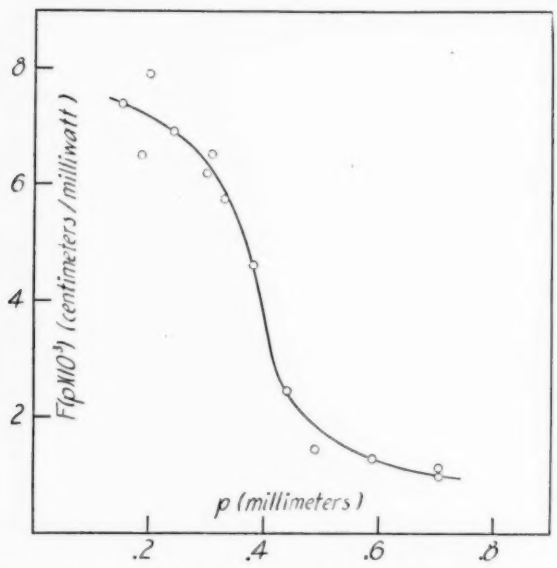

FIG. 6. Deflection per unit power input $F(p)$ as a function of gas pressure p.

[8] Knudsen, Ann. d. Physik **6**, 129 (1930).

TABLE I.

V = negative potential of cathode with respect to space; α = accommodation coefficient; f = fraction of current carried by electrons; φ_+ = work function of cathode for positive ions; V_i = ionization potential of the gas; φ_- = work function of cathode for electrons.

	α		f	
V	$\varphi_+=0$	$\varphi_+=V_i-\varphi_-$	$\varphi_+=0$	$\varphi_+=V_i-\varphi_-$
35	0.681	0.463	0.588	0.615
65	.570	.480	.573	.612
95	.512	.449	.536	.563
125	.410	.365	.516	.532

$\alpha_{\text{ave.}}=0.491$; $f_{\text{ave.}}=0.567$.

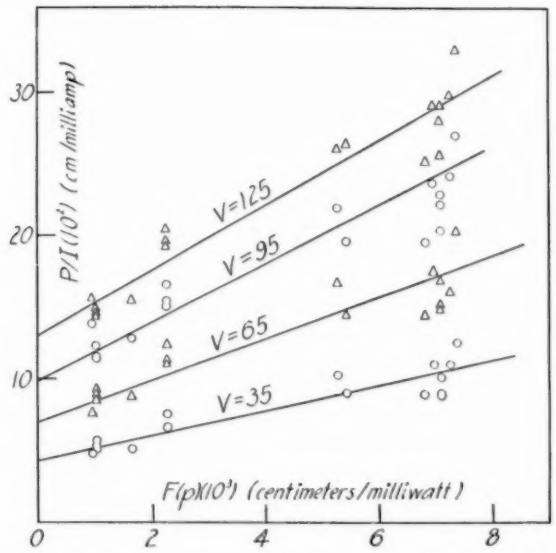

FIG. 7. Deflection per unit current to the cathode P/i as a function of deflection per unit power input $F(p)$ for different negative voltages.

If f is independent of the gas pressure p, then P/i should be a linear function of $F(p)$ by keeping V constant. Fig. 7 shows P/i vs. $F(p)$ for a series of different voltages. The slopes and intercepts were obtained by the method of least squares laying equal responsibility for error on abscissa and ordinate. From these slopes and intercepts, values of α and f were computed. An assembly of the results is given in Table I.

DISCUSSION OF RESULTS

The results in Table I were computed on the basis of two limiting values for φ_+ in estimating the radiometric effect, namely, $\varphi_+=0$ and $\varphi_+=V_i-\varphi_-$, where V_i is the ionization potential of the gas and φ_- the electron work function of the cathode. φ_+ has not been included in P_1 since its inclusion gives values of α intermediate between the other two. From the work of Oliphant[9] on the production of metastable atoms from positive ions reflected from a metal surface, it seems improbable that φ_+ could be as great as $V_i-\varphi_-$.

The calculations of f are subject to an uncertainty inherent in the apparatus which will now be discussed. It was possible for some ions to reach the back of the cathode through the clearance between the cathode and surrounding glass. Since these ions were trapped, they contributed nothing to the pressure P_1 and, since they probably lost most of their energy in collisions before reaching the cathode, contributed nothing to P_2. They were recorded as current, however, and therefore appeared as an increase in f. The cathode was slightly elliptical in shape, having major and minor diameters 1.30 and 1.23 centimeters. The clearance between cathode and glass was about 0.2 millimeter or about 6 percent of the total area. Since ions at the edge could reach the cathode in directions other than normal, the fraction of the positive ion current which reached the back of the cathode was probably somewhat greater than 6 percent (10 percent being a reasonable estimate). The values of f given in Table I were computed on the assumption that 10 percent of the positive ions reached the back of the cathode.

The average value of f shown at the bottom of the column is in fair agreement with the high values obtained by Harrington[10] is a continuation of work by Uyterhoeven and Harrington[11] on the fraction of current carried by electrons.

The values of f given in the table represent average values taken over different gas pressures and arc currents. Recent work reported by Found and Langmuir[12] would indicate that in neon, f is not constant as the arc current is varied, so that our procedure in reducing observations to a function of P/i should not be accurately justifiable. In the work reported here observations were made at constant gas pressure over as wide a range of arc currents as the apparatus would permit (a factor of never more than three). Within our limits of accuracy no change in P/i was observed, so that our procedure would seem to be justified for our purposes. However, a possible effect to be described below might have compensated to some extent for such a variation, if present. The apparatus did not permit a direct test of the constancy of f as gas pressure varied.

The second uncertainty in the results is as

[9] Oliphant, Proc. Roy. Soc. **A124**, 228 (1929).

[10] Harrington, Phys. Rev. **38**, 1312 (1931).

[11] Uyterhoeven and Harrington, Phys. Rev. **35**, 124 (1930).

[12] Found and Langmuir, Phys. Rev. **36**, 604 (1930); Phys. Rev. **39**, 237 (1932).

follows. If there are collisions within the sheath so that the energy gained by a positive ion in falling through the sheath is carried to the cathode by more than one particle, although the energy reaching the cathode is probably unaltered, the momentum for a given energy is increased. The pressure P_2 resulting from the heating by the energy delivered is therefore probably unaltered. The pressure P_1, however, which results from the momentum delivered should be increased. Thus when the sheath thickness (measured in mean free paths for the positive ions) is large, P_1 should be large. This condition should be realized for low currents, high voltages and high pressures. The effect of such a phenomenon would be to cause an apparent decrease in α for an increase in voltage. The results show such an effect. The sheath thicknesses were in some cases as much as five kinetic theory mean free paths thick and thus this effect should be expected, although Dempster[17] and others have found surprisingly long mean free paths for positive ions.

TABLE II. *Accommodation coefficients of neutral helium atoms.*

Metal	t°C	α	Reference
Pt	−100	0.49	(13)
	+200	0.37	(13)
	20	0.34	(14)
W	20	0.06	(15) (clean)
	50	0.53	(16) (dirty)
	50	0.17	(16) (clean)

[13] Soddy and Berry, Proc. Roy. Soc. **A84**, 576 (1911).
[14] Knudsen, Ann. d. Physik **46**, 641 (1915).
[15] Roberts, Proc. Roy. Soc. **A135**, 192 (1932).
[16] Michels, Phys. Rev. **40**, 472 (1932).
[17] Dempster, Proc. Nat. Acad. Sci. **11**, 552 (1925).

The values of the accommodation coefficient found by Compton and Van Voorhis for helium ions on molybdenum ranged from 0.35 at 36 volts to 0.55 at 126 volts. Since the ions are probably neutralized just before reaching the surface, ions and neutral atoms should behave alike when they strike a surface. Table II shows values of the accommodation coefficient for neutral atoms on various metal surfaces. Since the energies involved in the work of Compton and Van Voorhis and in the present work are much higher than those involved in any given in Table II, there is no reason to expect the values to be exactly the same. However, it is interesting to note the agreement. As one would expect, Table II shows an extreme sensitiveness of the accommodation coefficient to surface cleanness. In the present work it is believed that the continual bombardment of the surface by positive ions insured a reasonably clean surface. An interesting treatment of accommodation coefficients by K. T. Compton is soon to appear in the Proceedings of the National Academy of Sciences.

The results of this investigation, although subject to errors, seem definitely to prove that the rebounding neutralized ions exert a pressure on the cathode, give an estimate of the value of the accommodation coefficient and an estimate of the fraction of the current which is carried by electrons. These estimated values are of the same order of magnitude as values obtained by quite different methods. Compton's[2] theory that rebounding neutralized ions exert pressures of the order of those observed in various experiments is therefore verified directly (in the present work) and indirectly (in the work of Van Voorhis[3] and Compton).

The Effect of Foreign Gases upon the Relative Intensities of the Mercury Triplet $2\,^3P_{012}-2\,^3S_1$ under Conditions of Optical Excitation

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(Received July 26, 1932)

Effect of nitrogen and of mixtures of nitrogen and carbon dioxide upon the fluorescence of mercury vapor. By "stepwise" optical excitation, unexcited mercury atoms are raised to the $2\,^3S_1$ state. They may leave this level upon the emission of radiation by four paths—the first to the $2\,^1P_1$ state, a transition of relatively low probability, and the other three to the $2\,^3P_2$, $2\,^3P_1$, and $2\,^3P_0$ states with the emission of 5461A, 4358A and 4046A, respectively. Measurements, by totally independent methods, of the mean life of the $2\,^3S_1$ state yielded values, when measured by the line 5461A, equal to approximately four times those when measured by either 4358A or 4046A. Upon the addition of foreign gas, then, the intensity ratio of 5461A to either 4358A or 4046A should decrease with increasing pressure while that of 4046A to 4358A should remain constant. However, these ratios were all found to be invariant with pressure, up to 400 mm in the case of nitrogen and up to 100 mm in the case of the nitrogen-carbon dioxide mixtures.

INTRODUCTION

IF an energy level exists in an atom such that transitions to two or more lower levels are possible by the emission of radiation, the relative numbers of atoms which undergo these various changes are measured by the Einstein probabilities for the particular transitions involved. These probabilities are in general unequal for different transitions, but each is assumed to be a constant, entirely independent of both the method of excitation and the environment of the atom. Between the summation of these probabilities and the mean life of the state in which all the transitions originate there exists the relationship $\tau_n = (\Sigma_m A_m{}^n)^{-1}$. Using the methods of quantum mechanics, Sugiura,[1] Kupper,[2] Prokofjew,[3] and others have calculated transition probabilities for hydrogen and the alkali metals. According to their equations $A_m{}^n$, and therefore τ_n is a function of the quantum numbers n and l of the initial and final states of the atom emitting the light. This τ_n, however, is not necessarily the quantity measured by such experimental methods as have been used by Wien,[4] Kerschbaum,[5] Randall,[6] or Richter,[7] or involved in the quenching of fluorescence since the theoretical value is definitely associated with the time that the atom remains in the excited state whereas the experiments determine this τ_n or this mean life plus a time of emission of the quantum of light.

In this paper we are concerned with the mercury triplet $2\,^3P_{012}-2\,^3S_1$, the lines of which have the common upper state $2\,^3S_1$. According to the theory, the value of τ_n for this state should be the same whichever line is used for its determination. However, both Randall and Richter, independently and by two entirely different methods, found that the mean life of mercury atoms in the $2\,^3S_1$ state appears to be approximately four times as great when the 5461A radiation is observed as when either the 4358A or 4046A is studied. Randall's method consisted essentially in measuring the intensity of the radiations at various time intervals after its excitation. Richter has determined the mean life by a method due to Hanle,[8] who showed that it was possible to obtain these data very accurately from the rotation of the plane of polarization of fluorescent light and from the depolarization. Randall's results for the lines 4046A and 4358A checked within his experimental error at a value of $\tau = 5.75 \times 10^{-8}$ sec., while that for 5461A was four

[1] Sugiura, Phil. Mag. [7] **4**, 495 (1927).
[2] Kupper, Ann. d. Physik **86**, 511 (1928).
[3] Prokofjew, Zeits. f. Physik **58**, 255 (1929).
[4] Wien, Ann. d. Physik **73**, 483 (1924).
[5] Kerschbaum, Ann. d. Physik **79**, 465 (1926).
[6] Randall, Phys. Rev. **35**, 1161 (1930).
[7] Richter, Ann. d. Physik **7**, 293 (1930).
[8] Hanle, Ergebnisse der exakten Naturwiss **4**, 214 (1924).

times greater, $\tau = 2.37 \times 10^{-7}$ sec. According to Richter, the mean life, when measured by means of the line 5461A was 1.7×10^{-7} sec., by 4358A it was 4.6×10^{-8} sec., and by 4046A, 4.8×10^{-8} sec. In trying to explain these apparent discrepancies both Randall and Richter suggest that the life periods and transition probabilities may be different for the various hyperfine levels.

Whatever its explanation, the discrepancy in the values of τ_n for the $2\,^3S_1$ state of mercury is sufficiently striking to warrant testing its reality by another method. As is well known, collisions between excited atoms and the molecules of a foreign gas may result in de-exciting the atom before it has had an opportunity to radiate. Hence the addition of foreign gases to a fluorescing gas will quench the fluorescence and the quenching will be the more effective the longer the atom, on the average, remains in the excited state. If, then, the mean life of the upper state of 5461A is four times longer than that of the upper state of either 4358A or 4046A it would be expected that the intensity, in fluorescence, of 5461 would be reduced much more markedly by a foreign gas than that of either 4358 or 4046. More precisely, as the pressure of the foreign gas is increased the ratio of the intensity of 4358 to that of 4046 should remain constant, while $I(5461)/I(4358)$ and $I(5461)/I(4046)$ should decrease.

In order to determine whether or not this were so, the authors decided to study the effect of nitrogen gas over quite a pressure range upon the intensity distribution among the three components of the triplet as excited in fluorescence. In order to produce large changes in the intensity without materially increasing the pressure, mixtures of CO_2, a more efficient quenching agent, and N_2 were also included in the research.

Optical excitation was used as it was thought advisable to avoid any disturbing effects due to electrical fields.

Experimental Work

The apparatus, Fig. 1, was essentially the same as used by R. W. Wood.[9] However, a small brass cylinder whose ends contained 7 mm holes and which fitted snugly inside the cell, was placed within a few cm of the front plane face, and, as in

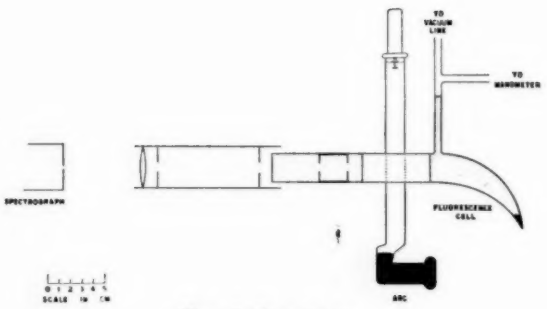

Fig. 1. Apparatus.

Wood's case, light baffles were placed in front of the cell. For the work with N_2 alone, a stream of air at about 27°C was led into the housing of the fluorescence cell to maintain a constant vapor pressure of mercury in the cell; but this was omitted in the case of the work with the N_2–CO_2 mixtures.

Eastman D.C. Ortho plates were used throughout this work and all were from the same batch. As the photographic intensity of the 4358A line was approximately ten times that of either of the other two, different lengths of exposure were necessary. The ratios of the intensities obtained in this research have therefore no absolute, but only a relative significance. A standardized procedure for the developing and fixing was followed so that comparisons from plate to plate might be made. They were calibrated by means of the usual "blackening curve" obtained by introducing calibrated screens, which were oscillated continuously, between the spectrograph and an arc, similar to the one used as a source of radiation for the fluorescence, whose intensity was diminished to approximately that of the fluorescence radiation by the introduction of frosted glass plates placed in line between the arc and the spectrograph. The plates were photometered with a Zeiss recording microphotometer. It was found necessary to photometer without any change of the settings of the instrument all those blackenings together with their calibration curve which represented the intensities of any one line for either the work with N_2 alone or for that with the mixtures, in order that comparisons be made from plate to plate.

Discussion of Results

The results of these experiments are given in Figs. 2–5. The data for N_2 alone are given in Figs.

[9] R. W. Wood, Phil. Mag. **50**, 774 (1925).

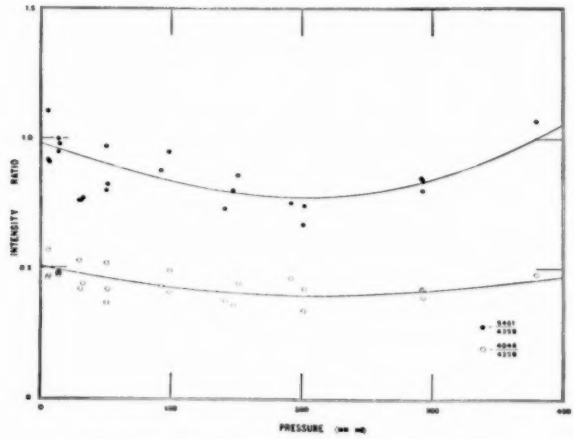

FIG. 2. Variation of intensity ratio with N_2.

2 and 3, while those for the N_2–CO_2 mixtures are given in Figs. 4 and 5. In Figs. 2 and 4 the values of the ratios $I(5461)/I(4358)$ and $I(4046)/I(4358)$ are given while Figs. 3 and 5 represent the data for the ratio $I(5461)/I(4046)$. The latter ratio was computed because the two lines involved were obtained simultaneously whereas 4358A was obtained separately. The possible advantage of

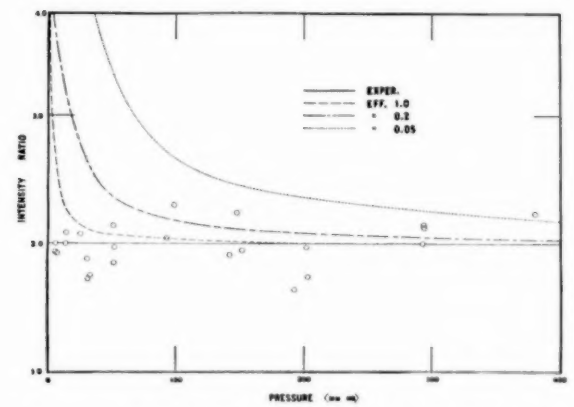

FIG. 3. Variation of intensity ratio $I(5461)/I(4046)$ with N_2.

this ratio lies in the fact that any irregularities such as slight variations in the time of exposure are eliminated. In the case of the N_2 data in Fig. 2 slight downward trends are discernible up to a pressure of approximately 200 mm of N_2 but from there on the trend is upward. The data for the N_2–CO_2 mixtures in Fig. 4, while not as consistent as those for the N_2 alone, show, as do those for N_2, that there is virtually no change in the ratios with increasing pressure.

Fig. 3 representing the data for N_2 alone, shows no trend at all in the value of the intensity ratio $I(5461)/I(4046)$, and the data for the same ratio in the case of the N_2–CO_2 mixtures, in Fig. 5, also yield a constant value with change of pressure.

Fig. 3 also contains three curves showing that which might be expected from considerations of

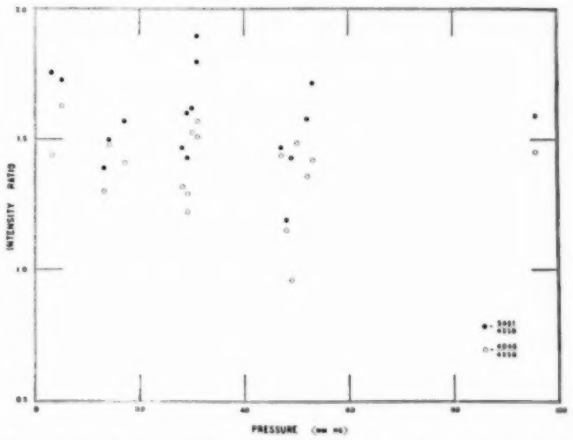

FIG. 4. Variation of intensity ratio with N_2-CO_2 (100–1) mixtures.

Richter's values of the life-periods, and of various damping efficiencies, as explained hereafter.

No data are available on the damping of the $2\,^3S_1$ level by foreign gases—in fact, the obtaining of such is almost an impossibility. The experimental procedure would have to be such that the manner in which the atoms were excited to the $2\,^3S_1$ level would not be affected by the inert gases whose quenching action was to be studied.

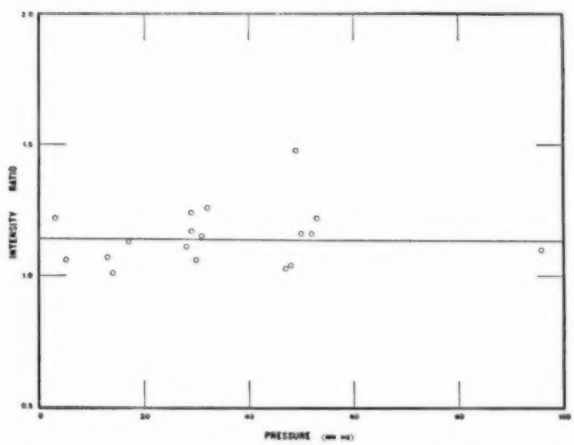

FIG. 5. Variation of intensity ratio $I(5461)/I(4046)$ with N_2-CO_2 (100–1) mixtures.

No satisfactory method for the obtaining of these data has so far been devised. However, Stuart[10] has investigated the damping action of various gases on the $2\,^3P_1$ state and his data have been recalculated by Gaviola.[11]

One assumption that may be made as to damping efficiency of N_2 on the $2\,^3S_1$ state is that this efficiency is comparable with that of argon on the $2\,^3P_1$. This efficiency, according to Gaviola, is 0.05. If this be true the variation of the ratio of the intensities of 5461A to 4046A would follow the curve Eff. = 0.05.

The assumption may be also made that the damping efficiencies of N_2 on both the $2\,^3S_1$ and $2\,^3P_1$ levels are equal. In this case the ratio of the intensities gives rise, according to the data of Randall and Richter, to the curve, Eff. = 0.2.

If all the kinetic theory collisions be effective we have a damping efficiency of unity and the variation of the ratio should follow the curve Eff. = 1.0.

The ratios were not determined at zero gas pressure because of the very low intensity of the fluorescence under these conditions. This would have necessitated longer exposures and consequently no direct comparisons could be made between the data obtained at the two different times of exposure. If the possibility of extrapolating the experimental data to zero gas pressure be assumed, theoretical curves may be drawn with the aid of the equation for damping and also of various assumed damping efficiencies. These curves show a rather sharp initial drop, falling below the experimental curve. In order to show that the experimental points do not correspond to the relatively flat portion of these theoretical curves the latter were shifted upwards so that the curve Eff. = 1.0 lay approximately coincident with the experimental curve at high pressures.[12]

Another estimate of the effect of the N_2 on the $2\,^3S_1$ level may be made from the fact that in order to produce comparable blackenings with N_2 pressures of 200 mm and of about 5 mm, it was necessary in the latter case to insert between the arc and the fluorescence cell a screen which transmitted but 15 percent of the incident light. In all probability, even though wire screens are neutral over quite a range the percentage transmission of 2536A was less even than this figure. If then the intensity of the 4358A radiation has dropped to about 1/6, the mean time between collisions is of the order of 1/5 of the mean life of the excited state. If Randall's value for the mean life measured by means of 5461A be correct, the intensity of this line would decrease to about 4 percent. This would mean that the intensity of 5461A would decrease to about 27 percent of that of 4046A, which corresponds to a value on the arbitrary scale used in the figure of 2.2 at the pressure 200 mm. This value would be given by an efficiency of approximately 0.1.

Examination of the data shows that there is no rise in the value of the ratio in the region of low pressure such as is demanded by the theoretical curves. In fact, below a pressure of 30 mm N_2, as shown in Fig. 3, *all* of the experimental points definitely lie below the curve which would be expected if all of the collisions were effective. Thus, the effect that is predicted from the values of the mean life of the $2\,^3S_1$ state, obtained by both Randall and Richter, has not been found in this research.

One possible reconciliation of this work to that of Randall and of Richter, which is, however, specific for this case, is the following. Under the conditions of the experiments of Randall and Richter it is possible that thermal equilibrium between the various hyperfine levels postulated by them is not attained during the lifetime of the excited state whereas in the experiments reported in this work the pressures of foreign gas used are such as to assure the attainment of such an equilibrium.

[10] Stuart, Zeits. f. Physik **32**, 262 (1925).

[11] Gaviola, Phys. Rev. **33**, 309 (1929).

[12] From the equation for damping it is obvious that the limiting ratio at high pressures, measured in absolute units, is unity and at zero gas pressure it is merely the ratio of the two life periods. The ordinates of the graph are purely arbitrary since no corrections have been made with respect to the sensitivities of the plate for the two lines.

Photoelectric and Metastable Atom Emission of Electrons from Surfaces in the Rare Gases

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(Received September 14, 1932)

The causes of conductivity observed at considerable distances beyond the end of a rare gas discharge are investigated at pressures of 0.5–2 mm. In pure gases, currents from negatively charged electrodes are found to be mainly caused by photoelectric action thereon of the resonance or other extreme ultraviolet radiations. For similar discharge conditions, currents are roughly 10-fold greater in Ne than in He and 20-fold greater in Ne than in A. When traces of impurities (ionizable by metastable atoms) are added, the currents are increased because of the ionization of the former by metastable atoms (volume effect). Under these circumstances strong irradiation with light of the gas in question (which is found to destroy more than half the metastable atoms formed) causes marked decreases in the currents; but the currents in pure gases are only negligibly so reduced. Electron currents from a thin metal disk are several times greater when the plane of the disk is perpendicular to the direction of the radiation than when it is parallel thereto. The fraction of the currents in Ne which may be caused by the emission of electrons from surfaces by metastable atoms is <10 percent for the parallel position of the above disk and <3 percent for the perpendicular position. This fraction is still smaller in A but may be considerably higher in He. The fraction of the scattered resonance quanta which are converted into metastable atoms before reaching the walls may be as high as 50 percent in He but is probably <5 percent in Ne. The small value of this fraction in Ne is in accord with other evidence for the abnormally long free paths of resonance radiation in this gas. The efficiency of metastable atom emission of electrons from surfaces under the present conditions is found to be $<<1$ and is probably not much greater in order of magnitude than the photoelectric efficiency of the radiations concerned. The effective cross section for the ionization of A by metastable Ne atoms is estimated. A convenient method of detecting and measuring small traces of impurities in Ne and He is described. Evidence is given that, on account of wall reflections, visible radiation, and probably also (but for gaseous absorption) extreme ultraviolet radiation, passing down a glass tube will, over a considerable range, decrease approximately with the inverse first power of the distance.

I. INTRODUCTION

THE present paper is an account of a study of the conductivity existing in a tube at a considerable distance beyond the end of a discharge in Ne, He or A, at 0.5–2 mm pressure. Langmuir and Found[1] showed that such conductivity in Ne cannot be accounted for by any agent moving away from the discharge by diffusion; they ascribed this conductivity to the emission of electrons from the glass walls and metal surfaces by metastable atoms[2] which they concluded were produced as a result of the absorption of the penetrating edges of the resonance lines.

The present experiments, already briefly reported,[3] confirm directly that many metastable atoms are produced at large distances (10 tube diameters or more) from the discharge, evidently by the method suggested by Langmuir and Found. The experiments show, however, that while these metastable atoms are of relatively great importance in causing conductivity in cases where a small amount of impurity ionizable by metastable atoms is present, their effects in pure gases are very small compared with the photoelectric effect of the extreme ultraviolet radiations.[4]

Penning[5] describes important studies of conductivity at higher pressures (40 mm) and confirms that large increases in conductivity which result when traces of A are added to Ne

[1] Irving Langmuir and Clifton G. Found, Phys. Rev. **36**, 604 (1930), and **40**, 129A (1932); Found and Langmuir, Phys. Rev. **39**, 237 (1932).

[2] M. L. E. Oliphant, Proc. Roy. Soc. **A124**, 228 (1929) and others.

[3] Carl Kenty, Phys. Rev. **38**, 377L (1931).

[4] Preliminary, briefly reported, measurements (Carl Kenty, Phys. Rev. **38**, 2079L (1931)) indicate photoelectric efficiencies for these radiations which are quite high—of the order of 1–5 electrons per hundred quanta for a clean Ni surface depending on the gas (whether He, Ne, or A) and the cleanliness of the surface.

[5] F. M. Penning, Zeits. f. Physik **78**, 454 (1932).

are caused by the ionization of A by metastable Ne. Duffendack and Smith[6] report recent studies of the conductivity in Ne and draw conclusions in accord with the present ones insofar as these overlap. Spiwak and Reichrudel[7] on the other hand, conclude that currents from a negatively charged probe in Ne are caused mainly by the emission of electrons therefrom by metastable atoms; their work will be referred to below.

II. Apparatus

In Fig. 1, K is a W filament serving as a cathode and A is a Mo anode. p_0-p_4 are W probes, 0.1 cm in diameter, and projecting 0.9 cm inside the tube. D is a W disk 1.88 cm in diameter and 0.025 cm thick; this is mounted

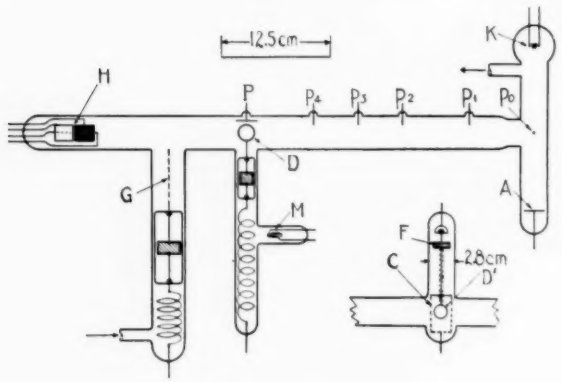

Fig. 1. Diagram of apparatus.

on a glass float as shown, containing a piece of Fe, so that it can be rotated by means of a magnet or moved back into the side tube for degassing purposes or for coating with Mg from a Mg gun M (for a study, to be reported later, of the variation of the emitted currents with the work function). P is a Mo disk, 2.5 cm in diameter, mounted with its axis in line with the axis of rotation of D. In the measurements to be discussed, D was adjusted in every case to a central position in the main tube where its edge was about 0.3 cm from P. G is a Ni gauze which can be moved magnetically to a position where it fills the main tube reducing the intensity of the radiation passing down the latter by a known amount (36 percent). H is a positive ion detector, of the type originated by Lawrence and Edlefson.[8] The use of this detector as well as the use of the gauze G, will be discussed below.

Another tube used is essentially similar to the one just described except that the disk is covered with mica on one side. In still another tube used, of the same general character, a thin Ni disk D' is suspended from a swivel joint so that it can be rotated inside a Ni gauze cylinder C, Fig. 1, by means of a magnet acting on the Fe strip F. The cylinder C, 2.5 cm in diameter, is made of Ni gauze having ten 0.022 cm wires per cm; it is closed at the top with a Ni disk, having a hole in its center. A quartz tube passes through this hole serving to insulate and center the disk inside the cylinder.

The tubes were of Pyrex and were degassed under exhaust for 2 hours at 450°C. The metal parts were degassed by heating inductively to incandescence. The Ne was purified by continuous circulation, in the direction of the arrows, over charcoal in liquid air; the He by circulation over chabazite in liquid air; and the A by the action (before the admission of the gas to the experimental tube) of a misch metal arc. Means were provided to prevent Hg from entering the tube. The presence of impurities in the gas (especially in the cases of Ne and He) was found to be of great importance. A method for conveniently measuring the purity of Ne and He was developed and used throughout the experiments; this method will be described in appendix A at the end of this paper.

III. Results in Pure Ne

a. Characteristics with disk perpendicular and parallel to axis of tube

In Fig. 2 curve 1 is the current between D and P (Fig. 1) in quite pure Ne at 1.5 mm pressure, as a function of the voltage applied between them when D is perpendicular ($\perp$) to the axis of the tube and a positive column discharge of 120 m.a. is maintained between K and p_2. Curve 2 is the current under the same circumstances when D is parallel ($\parallel$) to the axis

[6] O. S. Duffendack and R. W. Smith, Bull. Am. Phys. Soc. **7** [7] 8 (1932).

[7] G. Spiwak and E. Reichrudel, Phys. Rev. **42**, 580L (1930). See also F. Ludi, Zeits. f. Physik **76**, 319 (1932).

[8] E. O. Lawrence and N. E. Edlefson, Phys. Rev. **34**, 233 (1929).

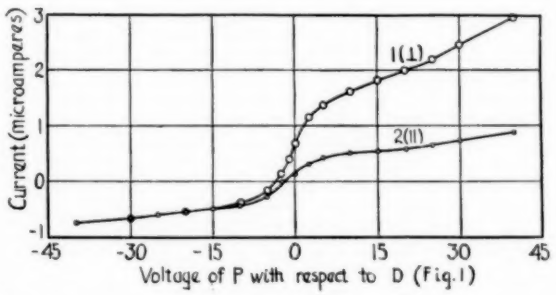

FIG. 2. Current voltage characteristics of electrode system $D-P$, Fig. 1.

of the tube. The electrode system is floating with respect to the discharge, here and in what follows.

Fig. 3 shows similar characteristics for the system $D'—C$ of Fig. 1 for two different pressures. The discharge is 120 m.a. between the cathode and a probe situated 10 cm from D'.

b. Interpretation of characteristics

Assuming that the currents in the preceding section are caused by an electron emission from the electrodes, the curves of Figs. 2 and 3 can roughly be broken up into three regions: (1) a region from 0 to say 7 volts (to take first the right-hand parts of the curves) where the currents are probably limited by the back diffusion of electrons;[9] (2) a relatively flat region, say from 7 to 20 volts, which may be taken to represent the saturation electron emission from D or D'; and (3) a region above 20 volts where the currents are increasing by cumulative ionization in the space. The same divisions presumably hold for the left-hand parts of the curves.

The approximate saturation currents in the region (2) above, measured with D or D' at the arbitrarily chosen potential of -15 volts with respect to P or C, respectively, and with conditions of pressure and discharge as in Fig. 2 unless otherwise specified, will be referred to below as I_s and I_p for the $\perp$ and $\parallel$ cases, respectively; the ratio I_s/I_p will be called R.

That I_s and I_p are actually the approximate saturation currents perhaps requires further justification. We note first that curves 1 and 2 of Fig. 3 show considerably more evidence of saturation than the other curves. This is to be expected since because of the relatively low pressure, both the back diffusion of electrons (at the lower voltages) and cumulative ionization (at the higher voltages) will be less important in this case. Also the higher electric field at D', due to the fact that the gauze cylinder totally surrounds it, will tend to decrease the effect of back diffusion in this case. Rough calculations, made on the basis of Langmuir's theory, indicate that even at the higher pressures (1.5–2 mm) back diffusion will not be of major importance in the voltage region (2) here discussed.

The currents in the present experiments are presumably too small to be limited by space charge.[10] We note that I_s is several times greater than I_p; this could not be so if I_p were already limited by space charge. Further, when a discharge of 120 m.a. was run between K and A, Fig. 1, instead of between K and p_2 as in the case of Fig. 2, curves similar to those of Fig. 2 were obtained and R was practically unchanged although the currents themselves were tenfold smaller.

It is seen from Fig. 3 that for the curves 1 and 2 the value of R is about 4.3. Considerably

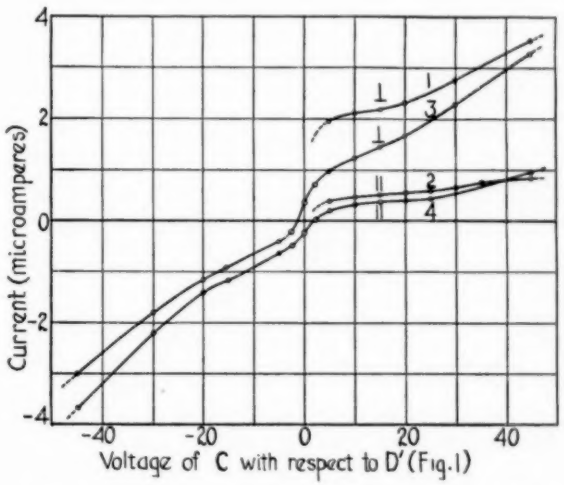

FIG. 3. Characteristics of electrode system $D'-C$ of Fig. 1. Curves 1 and 2 are for Ne at 0.5 mm pressure and curves 3 and 4 are for Ne at 2 mm pressure.

[9] Irving Langmuir, Phys. Rev. **38**, 1656 (1931).

[10] Penning, see reference 5, has found a space charge effect in cases where the currents are mainly due to ions and electrons formed in the space (impure gas) but we believe this is to be associated with the relatively very low mobility of the ions (as compared with that of the electrons in our case) especially at the much higher pressures in Penning's experiments (40 mm).

larger values were found for the mica-backed disk.[11] (§ II.) Since the geometry of the space surrounding D' is identical[12] for all orientations of D' (and the similarity of the curves and the merging together of the left-hand parts of the curves of Fig. 2, indicate that this is also approximately true in the case of D), and since space charge and back diffusion have been eliminated as unimportant,[13] the difference between I_s and I_p must represent a real difference in the electron emission from the disk in the two cases. This difference is easily explained as being due to the photoelectric effect of the primary radiation beam passing down the tube.[3, 4] If the currents considered were wholly due to the emission of electrons from D' by metastable atoms, R should be somewhat less than 1, instead of 4.3, since on account of the shadow cast by D' in the $\perp$ case less radiation (for the production of metastable atoms) will fill the cylinder in this case than in the $\parallel$ case.[14]

That the $\perp$ currents in the case of the *left-hand* branches of curves 3 and 4 of Fig. 3 should be less than the $\parallel$ currents follows naturally on the present views since in the $\perp$ case the disk casts a shadow on the inner rear surface of C, lowering the photoelectric emission therefrom, and at the same time cutting off the production of scattered radiation in the space in the region of the shadow (which might otherwise partly act photoelectrically on C and partly produce metastable atoms which would cause electron emission from C).

Assume, for the $\perp$ position, that

$$I_s = I_s^0 + I_s' + I_s'', \tag{1}$$

where I_s^0 is that part of I_s which is produced by the photoelectric effect of the primary beam on the front face of D', and I_s' and I_s'' are the currents caused by the scattered energy (as radiation or metastable atoms) incident on the front and back surfaces of D', respectively. Call I_p' that part of I_p caused by the scattered energy incident on one side only of D' in the $\parallel$ position. Further assume that the production of scattered energy in the space is uniform. Then if D' were small compared to the surrounding enclosure it would follow that

$$I_s'' = I_s' = I_p' \tag{2}$$

since the scattered energy reaching a given side of D' would not vary with the orientation of the latter. In the case of D of Fig. 1 this is fulfilled; for, on replacing D by another similar disk covered with a thin layer of mica on one side, I_p was found to be closely equal to I_s in the case where the uncovered face was turned away from the discharge. It is assumed that also in the case of D' and C, Eq. (2) will hold approximately. From Eqs. (1) and (2) it follows that

$$R = (I_s^0 + 2I_p')/2I_p', \tag{3}$$

from which, substituting $R = 4.3$ for the case of curves 1 and 2 of Fig. 3, it follows that $I_s^0 = 6.6I_p' = 6.6I_s'$. Thus the electron emission caused by the primary radiation flux incident on the front face of D in the $\perp$ case is 6.6 times as great as the emission caused by the random flux of scattered energy incident on the same surface. From this result and Eqs. (1) and (2) it follows about 77 percent of I_s is caused by the direct photoelectric action of the primary beam. Similarly in Fig. 2, R is about 3.3 and the corresponding percentage is 70. Results with the mica backed disk were entirely compatible with these results.

c. The effects of irradiation

If the region around the electrodes D and P (or D' and C) of Fig. 1 is strongly irradiated

[11] Cf. Found and Langmuir, last paper of reference 1, Fig. 10.

[12] Spiwak and Reichrudel (reference 7) attribute somewhat similar results to differences in geometry. Their grounds for this are not entirely clear to the writer; but in any case it is evident, as discussed above, that there is no difference in geometry in the case of the arrangement D' and C of Fig. 1.

[13] Even if back diffusion were important here the theory of this effect (reference 9) requires that the currents be proportional to the saturation emission.

[14] R at pressures of 1–2 mm in A and He (see § V) is found to be 25–50 percent less than the corresponding values in Ne. At pressures $< 1/2$ mm R is about the same in A as in Ne although still relatively small in He (the case of He is of special interest—see remarks in § V). R increases slowly with discharge current in Ne and relatively rapidly in A (e.g., from 1.4 to 3.5 as the discharge current, otherwise similar to that in Fig. 2, is increased from 20 to 200 m.a.). Now if the currents in the present experiments were mainly due to metastable atom emission, R should be roughly the same in all cases, and equal to or slightly less than unity.

with light from another Ne discharge tube,[15] the currents are only slightly affected, provided the gas is very pure, being decreased by small amounts[16] (2.5 percent in the case of I_p and <1 percent in the case of I_s). In impure gas, however, irradiation produced very considerable decreases in the currents (which had already been considerably increased by the added argon. See below).

Now Meissner and Graffunder[17] and Penning[18] have shown that metastable atoms are strongly destroyed by such irradiation. Experiments to be described below show that also in the present studies metastable atoms are so destroyed. The near absence of effect of irradiation on the currents (in particular I_p) leads us to conclude either (1) that metastable atom emission causes only a small fraction of I_p or (2) that if this process causes an appreciable fraction of I_p, its efficiency is nearly the same as the photoelectric efficiency of the scattered radiations. (2) follows since when metastable atoms are destroyed by irradiation, resonance quanta result[18] which we assume will follow the same laws of diffusion as the metastable atoms and hence have equally good chances of reaching a given electrode. Further experiments, now to be described, give (in effect) an estimate of the actual number of metastable atoms formed and help us to judge concerning (1) and (2).

IV. Study of the Rôle of Metastable Atoms

a. Ionization of impurities by metastable atoms

The effects on the currents I_s and I_p (as defined in § IIIb) of adding A to Ne are shown in Fig. 4.

Penning[19] showed that starting potentials in Ne are markedly decreased by adding small traces of A, and he ascribed this effect to the ionization of A by metastable Ne atoms. It is reasonable to attribute the increases of current in Fig. 4 to the same cause.

Fig. 4 shows that although I_s is about 3.4 times as great as I_p at zero A percentage, the

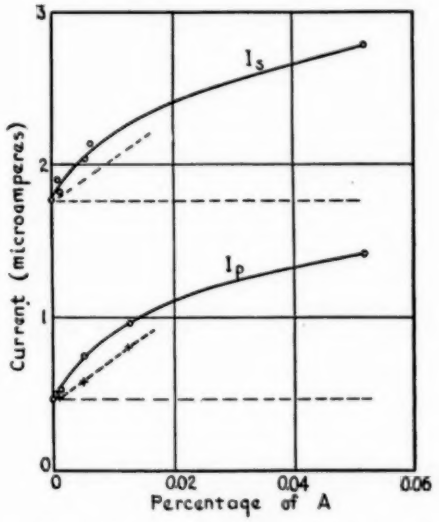

FIG. 4. The effect of A in increasing I_s and I_p. The broken lines show these currents as reduced by irradiation.

increments ΔI_s and ΔI_p, respectively, by which these currents are increased by a given A percentage are closely equal to each other. This indicates that the effect is caused simply by the sweeping out to the electrodes of the ions and electrons formed in the surrounding space by the process above discussed; for D is small enough, with respect to the surrounding space, that a roughly uniform concentration of metastable atoms would be expected to exist for both orientations of D.

The rate of production of ions, and hence $\Delta I_p(=\Delta I_s=\Delta I)$ should be proportional to the product of the concentration (N_A) and the metastable atom concentration (N_m). Thus, for A concentrations sufficiently small so that they

[15] Positive column discharge tubes 2 cm in diameter were used for this purpose containing Ne at about 1 mm pressure and carrying currents of about 3 amp. Only the region around the electrodes was irradiated, the remainder of the tube being shielded from the light. Photoelectric currents due to this external light itself were undetectable.

[16] It is probably significant that in the case of A (see below), where there are no common impurities ionizable by metastable atoms (except possibly O_2, see E. W. Pike, Phys. Rev. **39**, 534L (1932)), irradiation with strong A light produced no detectable effect on the currents whatever.

[17] K. W. Meissner and W. Graffunder, Ann. d. Physik **84**, 1009 (1927).

[18] F. M. Penning, Phil. Mag. **11**, 961 (1931) and a number of preceding papers.

[19] F. M. Penning, see reference 18. Penning also studied mixtures of other rare gases and impurities ionizable by metastable atoms and found similar results.

do not appreciably affect N_m, ΔI should be proportional to N_A; Fig. 4 indicates that this is experimentally the case. With higher A concentrations N_m will begin to be strongly reduced by the A and there will be no longer proportionality between ΔI and N_A. We would expect the curves to bend over with increasing A concentration, finally becoming horizontal when practically all the metastable atoms are being destroyed by the A; this the curves appear to do. It is assumed here, of course, that the rate of production of metastable atoms (which is dependent on the primary radiation reaching the region of the electrodes) is not appreciably altered by such A percentages as are here used. Evidence for this is the approximate constancy of $I_s - I_p$ which according to § IIIb represents the photoelectric action of the primary beam on D in the perpendicular position.[20]

It is well known that metastable atoms of Ne (and other gases) are strongly destroyed by even small traces of certain impurities. T. E. Foulke in unpublished work in this laboratory, has recently carried out experiments similar to earlier ones of De Groot[21] which show that under the circumstances of the present experiments, metastable Ne atoms were present in considerable numbers and that these were strongly destroyed by A. Foulke focussed, by means of a lens, a strong narrow beam of Ne light (from a special discharge tube furnishing an intense point source of light) on the region just beyond the end of a 100–200 m.a. positive column discharge in Ne (pressure 2–3 mm). Provided the gas were pure, the beam was strongly visible by light scattered by the metastable atoms. Under the best conditions the beam could be detected many tube diameters away from the end of the discharge. If, however, as much as 0.2 percent A was added to the Ne, the beam could no longer be detected even quite close to the discharge.[21]

Based on the assumption that N_m is reduced to half its value in pure gas by that amount of A which in Fig. 4 causes a ΔI_p which is half the apparent saturation ΔI_p approximate calculations indicate that the cross section for the ionization of A by metastable Ne is of the order of 0.4 times the normal cross section* (see remarks in Appendix A regarding H_2 and N_2).

b. Effects of irradiation in impure gas

In Fig. 4, the broken lines show the effects of irradiation on the currents I_s and I_p. It is seen that, for low A percentages, irradiation nullifies more than half of the increases in current (ΔI) which were caused by the addition of A. Since according to the views of the preceding section $\Delta I \propto N_A N_m$ it follows that N_m has been reduced by more than 50 percent by irradiation in these cases.

These conclusions have been confirmed by experiments in which ion concentrations were measured with the detector H of Fig. 1, and the effects of irradiation on these concentrations studied. The front cylinder of H was made of fine mesh Ni gauze so that radiation could pass through it. By use of the gauze G (described in

[20] Recent unpublished experiments carried out at the General Electric Research Laboratory, Schenectady, show that, for positive column discharges at such gas pressures and discharge currents as are here dealt with, the only effect on the visible lines of Ne of adding a small quantity (e.g., 0.1 percent) of A to pure Ne is to decrease the intensities of these lines by a few percent, the decrease being roughly the same for all lines; it seems reasonable to assume that also the intensities of the extreme ultraviolet lines here involved will not be altered by more than a few percent. See also Penning, reference 5.

[21] W. De Groot, Physica **6**, 53, 158 (1926).

* Briefly, solving the equation

$$D(d^2N/dr^2 + (1/r)dN/dr) + K - RN = 0$$

where N is the concentration of metastable atoms at a point distant r from the tube axis ($N=0$ at walls), D is the diffusion coefficient for metastable atoms and K and RN are the rates of production from resonance quanta and destruction by A, respectively, of metastable atoms per cm³, for $R=0$ and $R=1.76D$ cm^{-2} we find values of N at the axis in the ratio of $1 : \frac{1}{2}$. (Tube radius $a=1.7$ cm. For the solution of a similar equation see M. W. Zemansky, Phys. Rev. **34**, 213 (1929).) We assume from Fig. 4 that the latter situation occurs with about 0.02 percent A. Then employing the usual kinetic theory expressions for D (diffusion cross section assumed normal) and R (see E. W. Samson, Phys. Rev. **40**, 940 (1932)), we find $\sigma_i^2 = 0.37\sigma_0^2$ where σ_i^2 is the cross section for ionization in question and σ_0^2 is the normal cross section $(1.17\times10^{-8}$ cm $+1.43\times10^{-8}$ cm$)^2$. More correctly, half the metastable atoms will be used up by the A (say 0.02 percent) when the gradient of N at the wall is reduced by half. For such a reduction $R=2.7D$ cm^{-2} and we find $\sigma_i^2 = 0.57\sigma_0^2$. This estimate will be raised somewhat when the destruction of metastable Ne atoms in pure Ne by collisions with normal Ne atoms ($^3P_2 \rightarrow {}^3P_1$) and the reduction of the effective values of a by the electrodes are taken into account.

§ II) the response of H to positive ions was found to be roughly linear for the range of ion concentration dealt with.

The percentage reduction in I_p caused by irradiation as a function of A percentage, is shown in Fig. 5, which is drawn from the data used in constructing the curve I_p and the

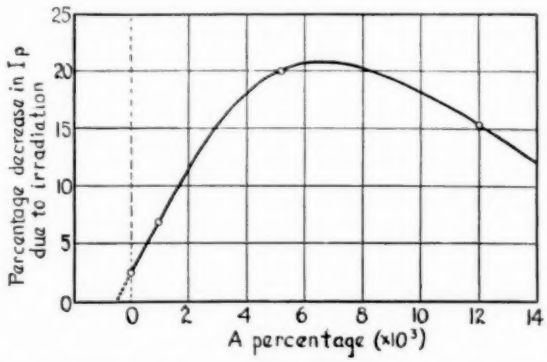

FIG. 5. Curve showing the effect of irradiation in decreasing I_p at different A percentages.

corresponding broken curve of Fig. 4. Fig. 5 shows the effect to pass through a maximum at about 0.0075 percent A, and to decrease with higher A percentages. Experiments have shown the effect to be very small at 0.2 percent A; here the destroying effect of irradiation will be small compared with that of the A. Under such circumstances two irradiation tubes gave roughly twice as much decrease as a single tube as would be expected if irradiation is here a small effect compared with other effects. At the lower A percentages (e.g., 0.005 percent) the second tube gave a much smaller decrease than the first; this is in agreement with the view, already arrived at by other means, that N_m is reduced markedly (50 percent or more) by irradiation under these circumstances.

Since at the point denoting zero A percentage in Fig. 5, the gas could scarcely have been entirely free from traces of impurities ionizable by metastable Ne atoms it would be interesting to know how closely the curve would approach zero in absolutely pure gas. If we knew (see § IIIc) that irradiation produced zero effect in absolutely pure gas, we could extrapolate the curve backward as indicated till it cut the horizontal axis and call this intercept the A percentage equivalent to the actual percentage of impurity in the tube.[22] Since we do not know this, all we can say is that this intercept probably represents the *maximum* impurity present, in terms of equivalent A percentage (in this case about 0.0005 percent).

c. Analysis of results

Suppose that Q resonance quanta are absorbed uniformly from the primary beam per cm³ per sec. in the region around D and P (Fig. 1), and that a fraction f of these are converted into metastable atoms before they reach the wall (see reference 26). Further suppose that a volume V surrounding D can be specified which will include all the absorbed quanta which diffuse to D. Such a surface, surrounding D, would be described by the locus of points of maximum radiation quantum (or excited atom) concentration. We shall assume as a first approximation that this same volume includes roughly also all the metastable atoms formed which diffuse to D. Then it follows that the saturation electron emission from D in the || position (I_p in pure gas) will be given by

$$I_p^0 = VQe[\alpha f + \beta(1-f)], \tag{4}$$

where e is the electronic charge. Now suppose that a sufficient concentration of A atoms is added so that all the metastable atoms are used up in ionizing them (we shall assume that this is the only important process by which the A destroys the metastable Ne atoms); and further suppose that all the ions and electrons so formed in a new volume, which we shall assume is M times as great as V, are swept out to the electrodes by the field. It follows that the current will be given in this case by

$$I_p^A = VQe[Mf + \beta(1-f)]. \tag{5}$$

In the case of Fig. 4 the current I_p appears to increase with added A to a saturation value 3 or 4 times as great as the original current; let us assume the value 4 as an upper limit. Then $I_p^A/I_p^0 = 4$ for this case from which by division

[22] F. M. Penning, Zeits. f. Physik **57**, 723 (1929), Fig. 4. Penning has pointed out (see reference 18, pp. 964, 965) how curves, somewhat similar to Fig. 5 above, which he obtained in studies of starting potentials, could be used as a method of detecting and measuring very minute traces of impurities in the rare gases. See also reference 5.

of Eq. (5) by Eq. (4) it is found, solving for f, that

$$f=3\beta/(M-4\alpha+3\beta). \quad (6)$$

In this equation β may be taken[4] to be of the order of 0.02–0.04. We do not know the value of M but we note that it will have the value 2 in the ideal case of plane parallel electrodes large enough so that edge effects can be neglected and provided the field is great enough to overcome the ionic space charge effect described by Penning.[10] In the actual case of electrodes D and P of Fig. 1, M will probably be considerably greater than 2: we shall assume that it lies somewhere between 2 and 6. Assuming a number of different combinations of M and β, f in Eq. (6) has been calculated for various values of α and the results are shown in Fig. 6.

Consider for example, the point $f=1$, on the curve ($M=4$, $\beta=0.02$), Fig. 6. At this point,

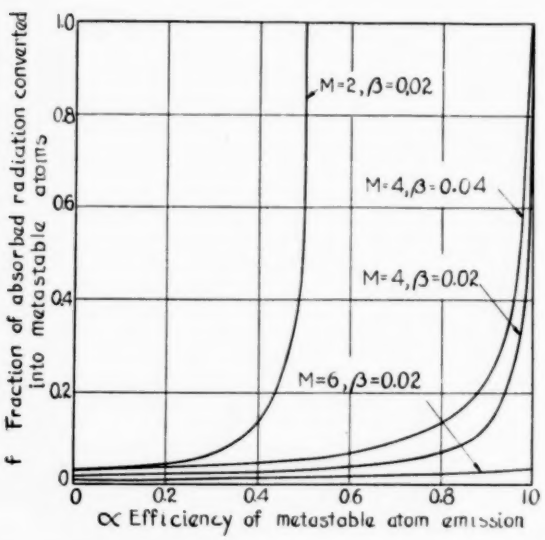

FIG. 6. Plots of Eq. (6) for a number of assumed sets of values for M and β.

$\alpha=1$, which by Eq. (4) means that I_p^0 would be wholly due to metastable atom emission; this would conflict very seriously with the irradiation experiments; for, if it were true, irradiation should have decreased the current by 50 percent or more instead of the actual 2.5 percent (§ IIIc). At the point $f=0.0164$, $\alpha=0.1$, Eq. (4) shows that about 8 percent of I_p^0 would be due to metastable atom emission. Now if half the energy of the metastable atoms is converted into radiation by irradiation (as follows from § IVb) the effect will be to reduce f in Eq. (4) by half; hence, by substituting first ($\alpha=0.1$, $f=0.0164$) in Eq. (4) and then ($\alpha=0.1$, $f=0.0082$) it is found that we would expect I_p^0 to be decreased by 3.5 percent by irradiation instead of the observed 2.5 percent. Thus this point would appear to be eliminated. However, this elimination process cannot justifiably be continued much further along this curve until experiments can be carried out, with gas of still greater purity than was obtainable in the present experiments, to ascertain just how nearly the effects of irradiation in such gas will approach zero.

Similarly, all the parts of all the curves can be eliminated except small regions to the extreme left. The conclusion has been drawn that f probably lies somewhere between 0.01 and 0.04, that α lies somewhere between 0 and 0.20,[23] and that the fraction of I_p^0 caused by metastable atom emission lies somewhere between 0 and 0.1.

It has been assumed above that all the metastable atoms formed in pure Ne reach the walls and electrodes and that none are destroyed by collisions of the first kind with normal Ne atoms. Now according to Penning[24] about 1 collision in 10^5 between a metastable atom and a normal atom will raise the former to the nearby resonance state (only the lower metastable level is here considered as it will probably be of preponderating importance). If λ_m is the mean free path of the metastable atom, the number of collisions made before such an atom reaches the walls will be $(a/\lambda_m)^2$ in order of magnitude[25] where a is the radius of the tube. In the

[23] E. W. Pike, Phys. Rev. **40**, 314L (1932) and private communication, has deduced from experimental results of Penning that α (Pike's λ) for Ne and for an Fe surface is probably not very different from β. As Pike, Phys. Zeits. **33**, 457 (1932) has pointed out, such a low value of α in the case of slow (room temperature) metastable atoms is not incompatible with the apparently high value of α for high-speed (800–1200 volt) He metastable atoms found by Oliphant (reference 2), in view of the high reflection coefficient for slow metastable atoms indicated by Oliphant's results.

[24] F. M. Penning, Zeits. f. Physik **46**, 335 (1928) see particularly pp. 342, 343. Also see some remarks in this connection by Carl Kenty, Phys. Rev. **40**, 633L (1932).

[25] W. Harries and G. Hertz, Zeits. f. Physik **46**, 185 (1927).

present case $\lambda = 0.0081$ cm ($p = 1.5$ mm, $T = 18°C$) on the basis of a normal radius for the metastable Ne atom, and $a = 1.7$ cm, and it is found that on the average some 5×10^4 collisions will be made by a metastable atom before reaching the wall. Thus a metastable atom will be somewhat more likely to reach the wall (or electrodes) and there be destroyed than to be destroyed in the gas. This probability will be increased by the presence of the electrodes which in effect decreases a above. Let us take as an extreme case that in which the chances of being destroyed at the wall (or electrodes) and in the gas are equal. Then half the metastable atoms formed will be raised to the resonance state before reaching the walls, or electrodes and the energy of these will reach the walls or electrodes as resonance radiation. This can be taken account of by replacing f in Eq. (4) by $f/2$, Eq. (5) remaining as before. Corresponding to Eq. (6) there is then obtained $f = 3\beta/(M - 2\alpha + \beta)$. By substituting $\beta = 0.02$ and $M = 4$, for example, in this expression, it is found by the previous methods that the upper limits for α and f allowed by the irradiation experiments are about 0.2 and 0.0166, respectively, as against the limits previously found for this case of 0.1 and 0.0164. Thus the effect of collisions of the first kind will be mainly to raise the upper limit for α.

It can be also readily verified that if the true saturation current in pure gas is somewhat greater than I_p^0 (see § IIIb) the effect will be mainly to increase the allowable value of α; and that if an appreciable fraction of I_p^0 is caused by the photoelectric action of light reflected from walls (see Appendix B) as appears probable from recent experiments in which light from a quartz Hg lamp were admitted to the tube through a quartz window, the effect will be mainly to increase the allowable value of f. However, it can be verified that none of these possibilities increase appreciably the maximum fractions of about 10 percent of I_p^0 and about 3 percent of I_s^0 attributable to metastable atom emission.

By choosing an experimental arrangement of simpler geometry (calculable M value), eliminating wall reflections, attaining higher gas purity and by taking other precautions it should be possible, by the present method, to improve considerably the estimates of α and f. Attempts in this direction are now in progress.

d. Some remarks concerning f

Based on the result of the preceding section that f is probably small (1–4 percent) rough calculations which have already been referred to[26] indicate that the mean free paths of the scattered radiations in Ne are much greater than are usually thought of for resonance lines[27]; for otherwise little scattered energy would reach the walls except as excited or metastable atoms. This result is in accord with thermopile measurements to be reported in a later paper which show that in Ne the extreme ultraviolet radiations penetrating large distances in a tube comprise a considerable fraction[4] of the total radient energy reaching the same distance. Heating experiments showed that the breadth of the lines is not governed, in these experiments, by the Doppler effect; further, the ion concentration in the discharges used are probably much too small to give broadening by the Stark effect; hence it is inferred[28] that coupling or some other form of pressure broadening,[29] present every-

[26] Carl Kenty, Phys. Rev. **40**, 633L (1932). In this calculation it was assumed that $f = (a/\lambda)^2 b\tau(v/\lambda_m)$ where a is the tube radius (1.7 cm), λ is the average free path (see paper, reference 27) of the scattered quantum, b is the efficiency of collisions changing resonance atoms into metastable atoms, τ is the mean life of the resonance state, v is the mean thermal speed of the atoms and λ_m is the mean free path of the atoms (assumed to be the same for resonance atoms as for normal atoms). The quantity $(a/\lambda)^2$ represents (see reference 25) roughly the number of free paths made by a quantum before reaching the wall, and (v/λ_m) is the collision frequency; it will be evident that f as represented by the expression is the chance of a quenching collision taking place before the quantum reaches the wall. The values tentatively assumed for τ and b were, respectively, 10^{-7} sec. and $10^{-2}-10^{-3}$ (see paper, reference 27 for some remarks on b) from which, taking f as between 1 and 3 percent, λ came out to be of the order of 0.2–2 cm. This calculation may be taken to apply to the $^1S_0 - {}^3P_1$ resonance line and the lower ($^3P_2$) metastable state.

[27] The discrepancy appears to be too great to be accounted for by a consideration of the effect of Doppler broadening on the radiation diffusion process—see Carl Kenty, Phys. Rev. **42**, 823 (1932).

[28] Carl Kenty, Phys. Rev. **42**, 823 (1932) and **40**, 633L (1932).

[29] J. Holtsmark, Zeits. f. Physik **34**, 722 (1925). For other references see footnotes 22 and 23 of first-mentioned paper of reference 28.

where in the tube, is the cause of the long mean free paths.[30] Direct evidence that the extreme ultraviolet Ne lines scattered in a side tube have abnormally long free paths (probably comparable with the tube diameter or larger) have recently been obtained, in unpublished work, by Langmuir and Found.

V. Argon and Helium

A and He at pressures of 1–2 mm give values of R (see § IIIb above) 25–50 percent less than those obtained in Ne, indicating that the radiations involved are more highly absorbed in these gases. In accord with this is the result that I_s is only about 0.05 times as great in A as in Ne, for similar discharge currents, and about 0.1 times as great in He as in Ne. It may also be, of course, that extreme ultraviolet radiations are developed with relatively less intensity in these gases than in Ne.

Preliminary experiments show that traces of Hg vapor added to A give the same kind of ionization effects as were noted in § IVa for the case of A added Ne. Irradiation (as in § IIIc, except using A discharge tubes) in pure A has no detectable effect on the currents I_s and I_p, although it decreases these currents provided a little Hg vapor is present. It is concluded by the methods of § IIIc that in this gas either (1) the current caused by metastable atom emission is entirely negligible or (2) α is closely equal to β and therefore of the order of 0.01 or 0.02.[4] The data were not complete enough to permit the application of the analysis of § IVc to be applied.

When A is added to He, the currents I_s and I_p increase relatively much more than in Ne. Preliminary curves (including those for irradiation) similar to the curves of Fig. 4 were taken for this gas at 1.5 mm pressure and the results when analyzed by the methods of § IVc indicate that (1) f may be as high as 50 percent,[31] (2) α may be as high as 0.1 or 0.2 and that (3) 20 or 30 percent of I_p^0 (i.e., 15–20 percent of I_s^0—see reference 14 regarding the relatively low value of R of about 1.5 in He) may be caused by metastable atom emission. Metastable atoms thus appear to be of considerably more importance in He than in Ne or A. Their presence at considerable distances beyond the discharge, and their destruction by A, were verified by scattering tests similar to those described in § IVa for Ne. (The scattered beam appeared greenish in color, evidently due to the absorption and reemission of λ5016A by singlet metastable atoms.)

VI. Discussion

Large values of R (§ IIIa) in Ne were obtained with the electrode system (like that of D and P, Fig. 1) only about $1\frac{1}{2}$ tube diameters from the end of the discharge where the metastable atom concentration was high enough to give a beam strongly visible by scattering. This suggests that some of the abnormality of size and lack of saturation, which has been observed[32] of currents to negatively charged collectors placed *in* discharges in the rare gases may be caused by the photoelectric effect. In any case the relative importance of metastable atom emission[32] in causing these effects seems likely to have been frequently overestimated.[3, 23] Oliphant[33] has recently reported experiments which seem to show that the greater part of these effects can be accounted for by the secondary emission of electrons by positive ions; it is perhaps significant that he found some evidence for an emission of electrons by some other agency than positive ions in Ne but not in the other gases (He or A) whereas by far the strongest photoelectric cur-

[30] It has been pointed out to the writer that we might expect the longer wave-length resonance line ($^1S_0 - {}^3P_1$) being an intercombination line, to have an abnormally long free path inasmuch as intercombination lines have generally been found relatively weak in absorption in elements of low atomic number.

[31] This result is in accord with the fact that in He metastable atoms can be produced spontaneously from singlet resonance atoms by radiation of the strong line λ20,582A whereas in Ne and A no such process is possible, transitions between resonance and metastable states being accomplished in these gases only by means of collisions of the first or second kinds (with probable small cross sections, see first-mentioned paper of reference 28).

[32] For bibliography see footnote 4 of reference 3. See also M. C. Harrington, Phys. Rev. **38**, 1312 (1931). Harrington points out that the method used by himself and Uyterhoeven does not distinguish between photoelectric and metastable atom emission. See also Found and Langmuir, reference 1.

[33] M. L. E. Oliphant, Proc. Roy. Soc. **A132**, 631 (1931).

rents were found in Ne in the present experiments.

Insofar as the resonance or other extreme ultraviolet radiations, like the visible radiations, may be strongly produced in the region of the negative glow, the results of the present experiments suggest that the photoelectric effect may play a rôle of more importance than has usually been recognized in contributing to the liberation of electrons from the cathode in the glow discharge in the rare gases.

It is a pleasure to record my indebtedness to Dr. Irving Langmuir, Mr. Clifton G. Found and Mr. T. E. Foulke for a number of stimulating conversations during the course of this work.

Appendix A

Method of detecting and measuring small quantities of impurities in Ne and He

The effect, discovered by Foulke (see footnote 2 of reference 3), that the conductivity in a side arm to a tube carrying a discharge in a rare gas is greatly increased by small quantities of impurities ionizable by metastable atoms, has been used to provide a convenient method of detecting and measuring small percentages of such impurities. In this method, the current to a probe situated several tube diameters from the discharge is measured under standard conditions of probe voltage, discharge current and total gas pressure, for different percentages of A or other impurity. The magnitude of this standard probe current (i_s) is then plotted against the known A percentage. Having once obtained such a calibration curve the percentage of A can then easily be obtained from i_s on any subsequent occasion. An example of such a calibration curve is shown in Fig. 7. Here the standard conditions adopted were:—Gas pressure: 1.5 mm discharge: 120 m.a. positive column type discharge between K and A (Fig. 1), probe (p_2) potential: -25 volts with respect to A. Small current differences (to the left of the curve) not representable on the scale of Fig. 7 were easily readable on the galvanometer used (sensitivity 10^{-8} amp. per mm). Such calibration curves were obtained by admitting small measured doses of A to carefully purified Ne by means of a dosing system employing only small Hg cut-offs and running the discharge only long enough to obtain the necessary readings (on account of a gradual clean-up of the A by the discharge).

At the standard probe potential the current varies only relatively slowly with the potential. This is shown in Fig. 8 where curve A represents a complete voltage-current characteristic for p_2 for the case of 0.0125 percent A. As the A percentage is decreased the positive currents decrease much faster than the negative currents

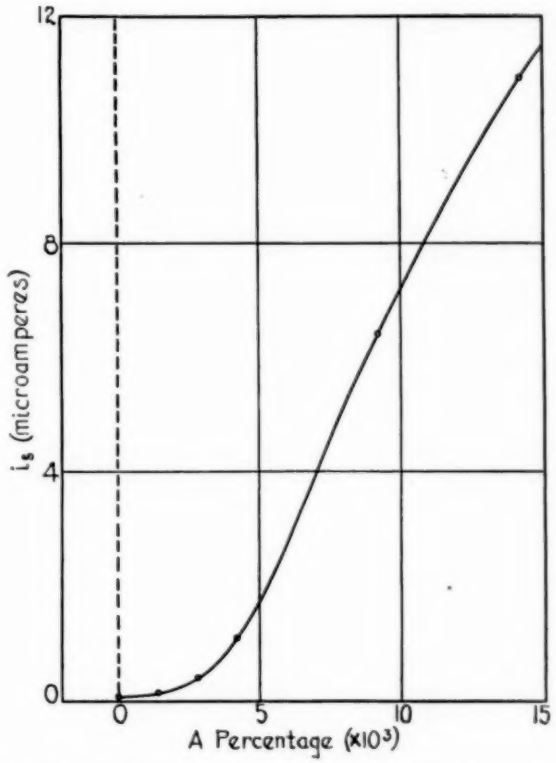

Fig. 7. Standard probe current as a function of A percentage.

until with the purest gas obtainable the two branches of the curve become nearly symmetrical.

Fig. 8 also shows the effect on the currents of strong irradiation on the space between the probe and the discharge (including the space around the probe).[34] The positive currents are decreased about 37 percent and the negative currents about 18 percent (effect not shown). If this percentage decrease in i_s is plotted

[34] Cf. C. G. Found and I. Langmuir, last-mentioned paper of reference 1, Fig. 9.

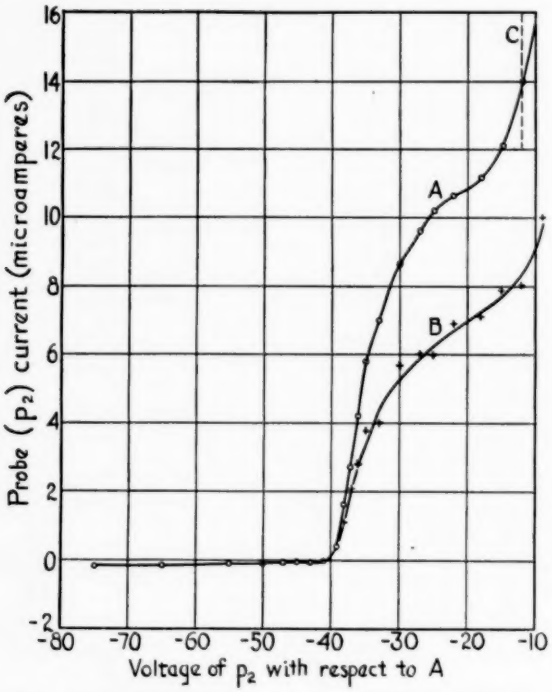

FIG. 8. Current voltage characteristics of probe p_2; *A*, without irradiation; *B*, with irradiation. A percentage 0.0125.

against A percentage a curve like Fig. 5 is obtained, which when extrapolated backward as in Fig. 5, indicates a maximum residual impurity at zero A percentage equivalent to less than 0.00025 percent A (compare § IVb).

The method has been used advantageously in the present experiments in keeping a check on the gas purity and in measuring A content; the state of gas purity could practically be read at all times from a dial. Such a rapid means of measuring impurity (e.g., A) content is especially desirable on account of the gradual (and sometimes fairly rapid) clean-up of the impurity by the discharge.

The upper limit of pressure at which the method is useful has not been determined but it has been found to lose its sensitivity rapidly at pressures much below 1 mm. The method has been used with He with success comparable to that obtained with Ne. With A as the main gas the method is of practical use only in detecting and measuring very small percentages of Hg. Small measured doses of H_2 and N_2 added to Ne gave i_s readings of the same order of magnitude as those obtained with similar doses of A, indicating cross sections for ionization of the same general order of magnitude in all these cases.

APPENDIX B

The effect of wall reflections on the transmission of radiation down a glass tube

Fig. 9 shows an example of the results obtained in an experimental study of the law of decrease of light intensity with distance inside a nonex glass tube of 2.5 cm internal diameter. In this study a thermopile was mounted at one end of the tube, the receivers of which substantially filled the whole field. A plane source of light filling the tube was approximated by mounting a small automobile headlight lamp 3 cm behind a white paper diffusing disk and movable with it. Distances were measured from the paper disk to the thermopile receivers.

It is seen from Fig. 9, curve A, that inside the glass tube the total intensity falls off quite closely according to the inverse first power of the distance (slope of curve 0.97 over the range 10–60 cm, which was as far as the measurements were carried out. Curve 2 shows that, without

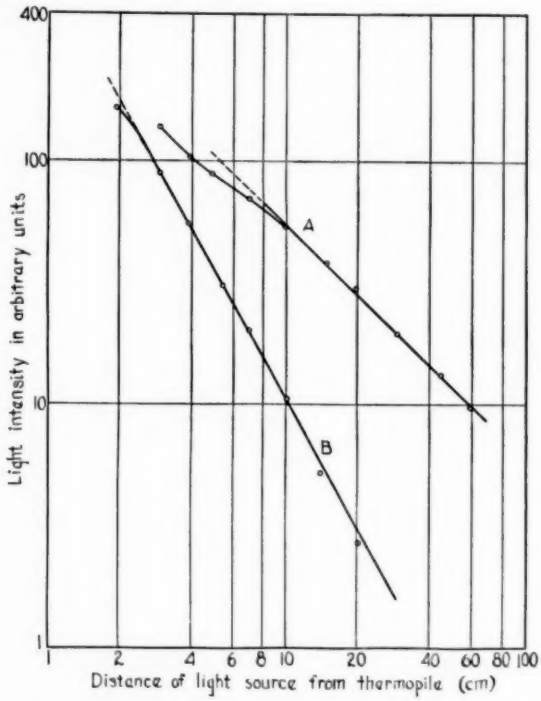

FIG. 9. Curve A: the rate of decrease of light intensity, with distance from the source, inside a glass tube. Curve B: the same without the glass tube.

the glass tube, the expected inverse square law was practically obtained; the line has the slope 1.9 over the range 4–20 cm which was as far as these measurements were carried out. On account of the finite size of the source the inverse square law would not be expected to hold at distances smaller than 4 cm. That the line has a slope 1.9 instead of 2 may be explained in that the apparatus was not completely removed from reflecting objects.

By comparison of curves A and B of Fig. 9 it is found that at 40 cm distance the effect of the glass tube is to increase the intensity more than 20-fold.

By placing a sheet of white paper over the end of the glass tube instead of the thermopile the intensity of illumination appeared quite uniform.

By comparison of the reflection coefficients for glass at small grazing angles of λ770A as found by O'Bryan[35] and similar reflection coefficients (somewhat less) for the radiations used here as calculated for unpolarized light by use of Fresnel's equations, it is concluded that, but for absorption in the gas, the resonance radiations in the present experiments would fall off with the distance even more slowly than according to the inverse first power. This helps to account for the unexpectedly large effects at considerable distances from the discharge.

[35] H. M. O'Bryan, Phys. Rev. **38**, 32 (1931).

Atomic Energy Levels and Zeeman Effect

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(Received December 5, 1932)

The present theory of complex spectra, neglecting magnetic interactions *between* electrons, has been successful enough in interpreting the data for certain simple configurations that it is of interest to discuss the extent to which this procedure can be applied to the energy levels and Zeeman effect of other configurations. The theory is extended to include p^5p and comparison is made with experimental data. Greater discrepancies appear here than in simpler cases. This is an example of the greater importance of the neglected interactions in more complex configurations.

THE theory of complex spectra, in the approximation which has as yet been most useful in correlating energy differences and g-values in simple configurations, accounts for the electrostatic and the largest electromagnetic energies. It makes use of angular integrations, leaving radial integrals as parameters to be determined by fitting part of the experimental data, some other data to be "predicted" thereby. The theory might be perfected by including all interactions,[1] but that must encumber it with more parameters and require more of the data for their determination, so is not desirable except where the simple approximation fails. We wish here to suggest that the neglected inter-electronic magnetic interactions become of greater importance with increasing complexity of configuration, and to show that even in the case p^5p the present approximation is only partially satisfactory.

I. SECULAR EQUATIONS FOR p^5p

The secular equations are very similar to those for the configuration pp' given by Johnson.[2] They are, however, slightly simpler, involving one less parameter, because of the fact that application of the Slater[3] method, as carried out by one of us and Shortley,[4] here gives two relations between the multiplet energies of (LS) coupling, rather than one relation as in pp'. To obtain the equations for p^5p we substitute γ for β in the secular equations* for pp'. Then the parameters for p^5p may be expressed in terms of Slater's radial integrals[3] ($F^2/25=F_2$) and represent the extreme-coupling multiplets as follows:

$$^3D\colon\ 0, \qquad ^1D\colon\ \alpha=12G_2,$$
$$^3P\colon\ \gamma, \qquad ^1P\colon\ \gamma=6F_2,$$
$$^3S\colon\ -\tfrac{3}{2}\gamma, \qquad ^1S\colon\ \delta=-9F_2+6G_0.$$

The matrices of spin-orbit interaction remain the same in p^5p, as Shortley[4] has shown, but we now expect to find the sign of the larger parameter (for p^5) negative.

[1] The first step in this direction has been made by H. C. Wolfe (Phys. Rev. **41**, 443 (1932)) who accounts for the interaction of the type (spin of one electron)—(orbit of other) in the simplest configurations. The still-neglected spin-spin interaction is smaller but of the same order of magnitude in the helium triplet. See also H. C. Brinkman, Zeits. f. Physik, *in print*.

[2] M. H. Johnson, Jr., Phys. Rev. **38**, 185 (1931).

[3] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[4] G. H. Shortley, Phys. Rev. **40**, 185 (1932). To visualize the here-pertinent result, we may derive it in the following abbreviated manner, similar to the well-known explanation of the inverted multiplet of an almost-closed shell. A closed shell has electrons $a^1\cdots a^6$, say, and we consider electrostatic interaction between them and, for example, one other electron b. The sum of these interactions is a constant. To calculate (within a constant) the interaction of $a^1\cdots a^5$ with b, consider a representation in which the sums $m_l^1+\cdots+m_l^5=m_l$ and $m_s^1\cdots m_s^5=m_s$ are diagonal; then removal of a^6, which has quantum numbers $-m_s$, $-m_s$, decreases the interaction by an amount calculated by Slater[3] for the quantum numbers $-m_l$, $-m_s$, m_l^b, m_s^b. (The interaction of a^6 with the other a's is independent of m_l, m_s.)

* In Johnson's paper,[2] in the nondiagonal terms of the energy matrix for $J=0$, a_1+a_2 should appear in place of a_1-a_2, as has been kindly called to our attention by Dr. Brinkman and may be verified by reckoning the energies for (jj) coupling, e.g. The consequent *small* change in the energies for $J=0$ has been made in Table I.

II. Determination of the Parameters

The five parameters were so evaluated as to make satisfactory agreement with the following experimental energies: the three levels with $J=2$, the two levels with $J=0$, and the sum of the energies for $J=1$; the $J=3$ state having been chosen as the zero level. The values so selected are: $a_1=40$, $a_2=-403$, $\alpha=537$, $\gamma=946$, $\delta=3084$. The solutions of the secular equation for $J=1$, with these parameters, are given in Table I, together with the g-values calculated with the help of formulas to be developed in §3.

That determination of the parameters is an obvious extension of previous applications of the theory. It is not, however, an adequate test of the subordination of the neglected magnetic interactions, since we cannot be sure that a parameter so determined really represents only the interaction it is intended to represent. A more severe indication of the importance of the neglected interactions is the fact that the magnetic parameters calculated for this configuration from the spectra of quite similar atoms[6] differ from those determined above, and lead to much worse disagreements of energy levels (though the g-values are about as good). Otherwise such calculation would constitute a more practicable determination of the parameters, leaving more data to be predicted.

Table I. *Energy levels and g-values for Ne, $2p^5 3p$.*

J	W (cm^{-1}) obs.[5]	W (cm^{-1}) calc.	g' obs.[5]	g' calc.
0	3313.7	*3292*	0/0	0/0
1	1381.4	1376	1.340	1.402
0	1260.4	*1282*	0/0	0/0
2	1201.5	*1201.5*	1.301	1.378
1	1115.1	1151	0.999	1.046
2	658.8	*729*	1.229	1.142
1	464.6	370	0.6695	0.627
2	167.2	*128*	1.137	1.148
3	*0*	*0*	1.329	(1.333)
1	−1399.2	−1328	1.984	1.907

III. Calculation of the Zeeman Effect

We apply the method given by Inglis and Johnson[7] to the configuration pp', using energy matrices given by Johnson.[2] We give the resulting formulas in the form for pp' so that they may be applied, if desired, to that configuration as well. They are to be modified for p^5p by substituting γ for β as in §1. For $J=2$ the coefficients of the transformation from (LS) to intermediate coupling (*vide* references 2 and 6) are:

$$R(k1)=\frac{1}{3^{1/2}}\left\{\frac{\alpha-2\zeta-W_k}{2^{1/2}\theta}\rho_k+\frac{\zeta}{\theta}\right\}R(k3),$$

$$R(k2)=\rho_k R(k3),$$

$$R(k3)=\left\{\frac{1}{3}\left(\frac{\alpha-2\zeta-W_k}{2^{1/2}\theta}\rho_k+\frac{\zeta}{\theta}\right)^2+\rho_k{}^2+1\right\}^{-1/2},$$

where $\rho_k=(1/2^{1/2})(\beta-W_k)/(\alpha-4\zeta-W_k)$;

$$\zeta=\tfrac{1}{4}(a_1+a_2);\quad \theta=\tfrac{1}{4}(a_1-a_2).$$

In terms of these, the g-values for intermediate coupling are

$$g_k'=(7/6)\{R(k1)\}^2+\{R(k2)\}^2+(3/2)\{R(k3)\}^2.$$

For the four states with $J=1$, the coefficients are more involved than heretofore:

$$S(k1)=\tau_k S(k4);\quad S(k2)=-(3^{1/2}/4\theta)(\sigma_k-3\gamma/2-2\zeta-W_k)S(k4);\quad S(k3)=\sigma_k S(k4);$$

$$S(k4)=\{\tau_k{}^2+(3/16\theta^2)(\sigma_k-3\gamma/2-2\zeta-W_k)^2+\sigma_k{}^2+1\}^{-1/2}$$

where

$$\sigma_k=\frac{1}{2(6)^{1/2}}\,\frac{(5\zeta+W_k)\{3(3\gamma/2+2\zeta+W_k)-8\zeta\}+5(3\gamma/2+2\zeta+W_k)\zeta}{5\zeta^2+(5\zeta+W_k)(\beta-\zeta-W_k)}$$

$$\tau_k=[1/(5\zeta+W_k)]\{(10/3)^{1/2}\zeta\sigma_k+(3^{1/2}/4\theta)(\sigma_k-3\gamma/2-2\zeta-W_k)\}.$$

The Zeeman effect for the states with $J=1$ is then given by

$$g_k'=\tfrac{1}{2}\{S(k1)\}^2+(3/2)\{S(k2)\}^2+\{S(k3)\}^2+2\{S(k4)\}^2.$$

Here (as also in other applications of this method) the g-values are best calculated by

[5] E. Back, Ann. d. Physik **76**, 317 (1925).

[6] By estimating slight alterations in effective nuclear charge, we have with sufficient accuracy $a_2=-520$ from Ne^+ $2p^5\,{}^2P$ or from Ne $2p^5ns$, and $a_1=8.6$ from Na $3p\,{}^2P$.

[7] Inglis and Johnson, Phys. Rev. **38**, 1642 (1931).

substituting in the formulas energy values, W_k, calculated from the parameters, rather than observed energies. Otherwise a single energy discrepancy may play havoc with a g-value, and with the g-sum. The formulas give g-values obeying the sum rule if "calculated" energies be used, as is easily proved.

IV. Limitations of the Present Approximation

Application of the theory to configurations having an s electron and an almost-closed shell (p^5s and d^9s) leads to experimental agreements ranging around 1 percent whereas the deviations in the two-electron configurations ps and ds average more than ten times as great.[8] This fact suggests[6] that the disagreements are due largely to neglected magnetic interactions between the electrons, since the usual magnetic (spin-orbit) energy should be relatively larger in p^5s than in ps, because of the larger nuclear charge effective in p^5s for the electrons having an orbital angular momentum. The excellent agreement[9] in cases involving almost-closed shells suggests that extension of the application should be most fruitful in the case of p^5p. Here one should indeed find a distinct superiority over the configurations pp', pd, etc. The situation is, however, not so favorable as in p^5s. The largest interactions and the over-all separation remain of the same order of magnitude, as do the neglected magnetic inter-electronic interactions. But here we have many more levels crowded into the same range, and we take into account an additional spin-orbit interaction which is probably of the same order of magnitude as the neglected interactions. The energy deviations bear about the same relation to the over-all separation as in p^5s, but the accuracy relative to the separation of adjacent lines becomes here much less.

For Zeeman effect, the orientation of the angular momenta is all-important. In p^5p in intermediate coupling, the spin and orbit of each electron are oriented by electrostatic forces—in general fairly large—and by magnetic forces. For the outer electron the neglected magnetic forces may be as large as the reckoned magnetic force. The orientations of the spin and orbit of the outer electron might thus behave quite otherwise than calculated, making a considerable error in the Zeeman effect. In the g-values of p^5d, etc., the outer electron plays an even more important rôle, and the neglected interactions should become even less negligible.

In all but the simplest configurations, in intermediate coupling, no exact results may be expected from the present approximation. (The same is true of (LS) coupling (Slater's case[3]), where overlapping of configurations is more common, but there the remedy is quite different.) Even with rough results, there remains the possible utility of deciding between uncertain identifications of spectral lines, and the satisfaction that the theory fulfills our expectations.

[8] W. V. Houston, Phys. Rev. **33**, 297 (1929); Laporte and Inglis, Phys. Rev. **35**, 1337 (1930); Condon and Shortley, Phys. Rev. **35**, 1342 (1930).

[9] The inconsistency of Pt and K^+ is directly attributable to interference of nearby configurations.

The Envelopes of Infrared Absorption Bands

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(Received December 19, 1932)

The *intensity formulae for the fine structure absorption lines of molecules of the symmetrical rotator type* are approximated by replacing the sums appearing therein by integrals. The resulting expressions are evaluated explicitly and may be used either to determine the intensity of an individual line or the envelope of all the fine structure lines. The envelopes of those bands corresponding to $\parallel$ type vibrations possess P, Q, and R-branches. The envelope may be characterized by two quantities, the relative intensity of the zero branch and the doublet separation which serve to fix the values of the moments of inertia A and C. The envelopes of the $\perp$ type vibrations are also determined and are plotted for a series of ratios of the moments of inertia. The range of validity of the approximation is discussed and the results applied to the infrared bands of the methyl halides. The doublet separations of the $\parallel$ type bands of these molecules are known and these (through the use of a plausible assumption regarding C) yield the following values of A, the moment of inertia $\perp$ to the symmetry axis. $A=32$, 61, 89, 99, $\times 10^{-40}$ for CH_3F, CH_3Cl, CH_3Br, CH_3I respectively. The distances between the carbon and halide nuclei are computed and compared with the corresponding distances deduced by Pauling. The agreement is satisfactory.

§1. INTRODUCTION

THE absorption bands of molecules in the near infrared region of the spectrum exhibit a fine structure because of changes in the rotational energy of the molecule which occur simultaneously with a change in the vibrational energy. In the case of diatomic molecules the positions of the lines and also their relative intensities may be expressed in a very simple manner. By neglecting interaction terms, which are usually small, the positions of the lines are given by $\nu=\nu_0\pm Jh/4\pi^2A$, where J may take the values 1, 2, etc. The intensities of the lines on the high-frequency side of ν_0 are proportional to $Je^{-\sigma J(J-1)}$, while those on the low-frequency side are proportional to $Je^{-\sigma J(J+1)}$, where $\sigma=h^2/8\pi^2AkT$.

In the case of the symmetrical rotator molecule (a molecule two of whose principal moments of inertia are equal, *viz.*, $A=B\neq C$) the positions and intensities of the fine structure lines may also be given explicitly.[1] The form in which the intensities are expressed is neither as simple nor as convenient to use as that for the diatomic molecule, since the formulae involve sums and double sums over a number of terms which may be large. These sums may be approximated by definite integrals, and it is the purpose of the present paper to evaluate these integrals. We believe that these expressions will be found useful and that in most cases they will lead to sufficiently accurate values for the intensities. They do, however, possess certain limitations which will be discussed in the final section of this paper.

[1] Cf. D. M. Dennison, Rev. Mod. Phys. 3, 314 (1931). The squares of the amplitudes appearing on pp. 313 and 314 as well as the intensity formulae themselves should all be multiplied by the factor 4. This correction does not, of course, affect the relative intensities of the lines, but only their absolute intensities.

§2. THE PARALLEL BANDS

In most molecules of the symmetrical rotator type the vibrations may be divided into two classes. In one of these the electric moment oscillates along, or parallel to, the symmetry axis; in the other the electric moment oscillates perpendicular to the symmetry axis. It is very convenient to discuss the fine structures of these two classes of bands separately. (Even if bands were observed for which the electric moment oscillated neither wholly $\parallel$ nor $\perp$ to the axis this method would still be applicable.)

The rotational energy of a symmetrical rotator molecule is given by $W_r=(h^2/8\pi^2A)[J(J+1)+\beta K^2]$ where $\beta=(A/C)-1$. The selection rules for the $\parallel$ type bands are $\Delta J=\pm 1$, 0 and $\Delta K=0$. If ν_0 is the vibrational frequency the positions

of the fine structure lines are then given by the following expressions, where the interaction terms between vibration and rotation have been neglected.

$$+ \text{ branch } \nu_J^{J-1\ K}_{\ K} = \nu_0 + Jh/4\pi^2 A,$$

$$0 \text{ branch } \nu_J^{J\ K}_{\ K} = \nu_0,$$

$$- \text{ branch } \nu_{J-1}^{J\ K}_{\ K} = \nu_0 - Jh/4\pi^2 A.$$

The intensities of the lines may then be determined with the aid of the following expressions, where σ has the same value as that already given, and $[2]$ is a symbol equal to 1 when $K=0$ and equal to 2 when $K\neq 0$.

$$+ \text{ branch } I_J^{J-1} = rL \sum_{K=0}^{J-1} [[2](J^2-K^2)/J] e^{-\sigma J(J-1)-\sigma\beta K^2},$$

$$0 \text{ branch } I_J^J = 4rL \sum_{J=0}^{\infty} \sum_{K=0}^{J} [K^2(2J+1)/2J(J+1)] e^{-\sigma J(J-1)-\sigma\beta K},$$

$$- \text{ branch } I_{J-1}^J = (I_J^{J-1}) e^{-2\sigma J}.$$

For any given band rL is a constant which for convenience is split into two parts, r, which is a function of A and B, and L, which is independent of these constants. Thus

$$r = 1/(\sum g_{JK} e^{-W_{JK}/kT})$$

and

$$L = [8\pi^3 \nu_0 N/3ch](V_{\xi v'}^{v''})^2 (1 - e^{-h\nu_0/kT}).$$

It may be shown that L is equal to the sum of the intensities of all the fine structure lines.

The approximation which will now be employed is equivalent to assuming that the values of J and K for the states in question are large compared with unity. In this case the quantity $J(J+1)$ may be replaced by J^2, $2J+1$ by $2J$, etc., and the sums may be replaced by integrals. Thus the intensity of the zero branch is given by the double integral

$$I_0 = 4rL \int_{J=0}^{\infty} \int_{K=0}^{J} (K^2/J) e^{-\sigma J^2 - \sigma\beta K^2} dK dJ.$$

The intensity of the Jth line of the positive branch is, in the approximation, equal to that of the Jth line of the negative branch, and is equal to

$$I_J = 2rL \int_0^J [(J^2-K^2)/J] e^{-\sigma J^2 - \sigma\beta K^2} dK.$$

The constant r is determined by means of a double integral rather than a double sum and may be explicitly evaluated.

$$r = 1 \Big/ \int_{J=0}^{\infty} \int_{K=0}^{J} 4J e^{-\sigma(J^2+\beta K^2)} dK dJ = \sigma[\sigma(1+\beta)/\pi]^{\frac{1}{2}}.$$

It will be noticed that r is the approximate value of the reciprocal of the "Zustandsumme." L is a constant which is equal to the total intensity of the band, as may be seen by integrating over all the band lines.

The evaluation of the integrals determining I_0 and I_J may be carried out by standard methods. For I_0 the first integration, over K, may be rewritten with the substitution $K=Jt$ where J is now constant, and t is a variable running from 0 to 1. The integral becomes

$$I_0 = 4rL \int_{J=0}^{\infty} \int_{t=0}^{1} (J^2 t^2/J) e^{-\sigma J^2 - \sigma\beta J^2 t^2} J dJ dt$$

since the limits are constant the order of integration may be reversed, giving as a result

$$I_0 = \frac{L\{\log [\beta^{\frac{1}{2}} + (1+\beta)^{\frac{1}{2}}] - [\beta/(1+\beta)]^{\frac{1}{2}}\}}{\beta[\beta/(1+\beta)]^{\frac{1}{2}}}, \quad \beta > 0$$

$$I_0 = L/3, \quad \beta = 0$$

$$I_0 = \frac{L\{[-\beta/(1+\beta)]^{\frac{1}{2}} - \sin^{-1}(-\beta)^{\frac{1}{2}}\}}{-\beta[-\beta/(1+\beta)]^{\frac{1}{2}}}, \quad \beta < 0.$$

It is evident from these expressions that I_0 can be written as a certain fraction of L, which is a function of β alone, independent of σ.

The constant $\beta = (A/C) - 1$ has a range of values from $-\frac{1}{2}$ to $+\infty$. For a disk-shaped

molecule $\beta=-\frac{1}{2}$; for a spherical molecule $\beta=0$, and for a linear (e.g., diatomic) molecule $\beta=+\infty$. In the mathematical treatment the expressions containing positive values of β must be handled separately from those containing negative values. In general this leads to different functions of β (such as, for example, those giving I_0); these functions are, however, continuous at $\beta=0$, as one has a right to expect.

The expression for I_J involves only a single integration which may readily be evaluated according to the several ranges of β.

$$I_J=(L/\beta)[\sigma(1+\beta)/\pi]^{\frac{1}{2}}e^{-\sigma J^2}\left\{[(2\sigma\beta J^2-1)/J(\sigma\beta)^{\frac{1}{2}}]\int_0^{J(\sigma\beta)^{\frac{1}{2}}}e^{-u^2}du+e^{-\sigma\beta J^2}\right\} \quad \text{for } \beta>0,$$

$$I_J=(4/3)L\sigma(\sigma/\pi)^{\frac{1}{2}}J^2e^{-\sigma J^2} \quad \text{for } \beta=0,$$

$$I_J=(-L/\beta)[\sigma(1+\beta)/\pi]^{\frac{1}{2}}e^{-\sigma J^2}\left\{[(1-2\sigma\beta J^2)/J(-\sigma\beta)^{\frac{1}{2}}]\int_0^{J(-\sigma\beta)^{\frac{1}{2}}}e^{u^2}du-e^{-\sigma\beta J^2}\right\} \quad \text{for } \beta<0$$

The formulae just obtained give approximately the intensity of the Jth line. Some modifications may have to be made in the case of molecules possessing several like atoms, for here the weights will be influenced by the nuclear spins. Such modifications will usually not be difficult to perform.

The approximate intensity formulae depend on the assumption that J and K are both large. This condition will be best fulfilled for heavy molecules (i.e., molecules with large moments of inertia) where each band contains many rotational lines which are very closely spaced. In this case, however, the spectrometer may not be able to resolve the individual lines, but only determine their envelope.[2] We wish to show that the properties of this envelope will yield information concerning the moments of inertia of the molecule.

We shall first consider the intensity of the zero branch as compared with that of the whole band; the ratio function R is defined as $R=I_0/L$. It was shown earlier that the total intensity of the whole parallel band is equal to L; the ratio function R for the various ranges of β is thus simply the corresponding I_0, as given above, divided by L. This ratio has been calculated as a function of β and is plotted as such in Fig. 1. For a disk-shaped molecule, $\beta=-\frac{1}{2}$, the zero branch intensity is almost half that of the whole band. For a spherical molecule the intensities of the three branches are equal, $R=\frac{1}{3}$, and as β increases the zero branch intensity decreases steadily. In the limit where $\beta=\infty$ we have in effect a linear molecule, and $R=0$, as it should, because such a molecule shows no zero branch at all in its $\parallel$ type bands. Thus if the ratio R could be measured experimentally it would then be possible to determine β from Fig. 1.

We consider next the separation between the maxima of the positive and negative branches in the parallel bands. The doublet separation for the absorption bands of diatomic molecules is analogous to this, and is in fact a special case of the more general doublet separation to be discussed now.

The doublet separation may be connected with the values of J corresponding to the most intense lines of the positive and negative branches by

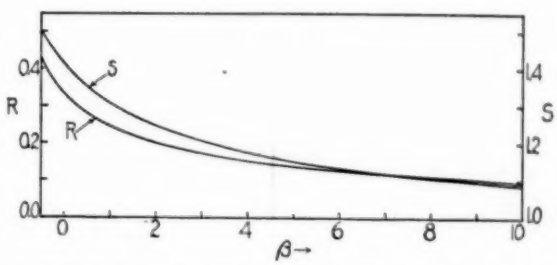

FIG. 1. The intensity ratio I_0/L for the zero branch and the separation function $S(\beta)$.

[2] Experimentally an infrared absorption band is determined by a curve giving the percentage transmission of the substance as a function of frequency. From these data a curve may be calculated giving the absorption coefficient P_ν as a function of ν. When the individual lines of the band are not resolved the value of P_ν found represents an average absorption coefficient and is equal to the average intensity of the lines in this region divided by the interval between them. In the present case the spacing of the lines is uniform and equal to α and therefore $P_\nu=I/\alpha$.

means of the following expression, where $\alpha=h/4\pi^2A$.

$$\Delta\nu=\alpha(J^+_{\max}+J^-_{\max}).$$

To the approximation being considered in this paper $J^+_{\max}=J^-_{\max}$ and accordingly $\Delta\nu=2\alpha J_{\max}$. The problem thus resolves itself into finding the number J of the most intense line. This may be done by setting the first derivative of I_J with respect to J equal to zero and solving for $J_{\max}$.[3] $J_{\max}$ and consequently $\Delta\nu$ is a function both of A and of β, fortunately, however, this function may be divided into two factors, the first of which, $S(\beta)$, contains β alone, and is simply connected with the root of the transcendental equation obtained by setting $\partial I_J/\partial J=0$, the second factor is the doublet separation for a diatomic molecule.

$$\Delta\nu=S(\beta)[(kT/A)^{\frac{1}{2}}/\pi].$$

The separation function, $S(\beta)$, is plotted as S in Fig. 1, it decreases from about 1.5 for $\beta=-\frac{1}{2}$ to $2^{\frac{1}{2}}$ for $\beta=0$ and approaches unity as β becomes infinite. The relation between S and β is given by the following empirical formula, which is accurate to within 0.5 percent for all values of β from $\beta=-\frac{1}{2}$ to $\beta=100$.

$$\log_{10} S=0.721/(\beta+4)^{1.13}.$$

The envelope of a single parallel band yields two data from which can be obtained the moments of inertia of the molecule under investigation. The ratio of the intensity of the zero branch to that of the whole band gives at once the value of β, by means of the ratio function R. This value of β determines the appropriate value of S to use in the above expression for $\Delta\nu$, which is the other experimental datum. The moment of inertia A is thereby determined, and this in conjunction with β gives the moment of inertia C.

When one of the moments of inertia is already known, the doublet separation can be used for finding the other. If A is known S can be calculated directly from the expression for $\Delta\nu$ and this in turn gives β, and hence C. If, on the other hand C is known, then the following expression will give β, and finally A.

$$S/(1+\beta)^{\frac{1}{2}}=[(\Delta\nu)\pi C^{\frac{1}{2}}]/(kT)^{\frac{1}{2}}.$$

§3. Perpendicular Bands

The perpendicular type bands are those bands for which the electric moment oscillates perpendicular to the figure axis. The selection rules of the rotational quantum numbers are $\Delta J=0,\ \pm1$, and $\Delta K=\pm1$. The fine structure lines for which $\Delta J=0$, $\Delta K=\pm1$ are multiple because the frequency of this transition does not depend upon the particular value of J. These lines are often called the zero branch lines and their intensities are given by formulae of the following type,

$$I^{J\,K}_{J\,K-1}=rL\sum_{J=K}^{\infty}[(2J+1)(J-K+1)(J+K)/2J(J+1)]e^{-\sigma[J(J+1)+\beta K^2]}.$$

The line whose intensity is given above has the frequency $\nu=\nu_0-(h\beta/4\pi^2A)(K+\frac{1}{2})$.

In the approximation to which we are working the intensity expression becomes

$$I_0=rL\int_K^{\infty}[(J^2-K^2)/J]e^{-\sigma(J^2+\beta K^2)}dJ.$$

The first part of the integrand may be integrated directly; the second part may be transformed into the logarithmic integral for which tables are available. In this way the intensity of the Kth zero branch line may be readily approximated,

$$I_0=(L/2)[\sigma(1+\beta)/\pi]e^{-\sigma\beta K^2}\left[e^{-\sigma K^2}+\sigma K^2\int_{\infty}^{\sigma K^2}u^{-1}e^{-u}du\right].$$

[3] In making the computations the substitution $z=J(\sigma\beta)^{\frac{1}{2}}$ was made, and the differentiation carried out with respect to z.

In order to obtain the envelope of the zero branch lines the quantity P, absorption coefficient, must be introduced. The position of the

Kth line (in our approximation) is $\nu=\nu_0+\alpha\beta K$, where $\alpha=h/4\pi^2A$. The spacing of the lines is uniform and equal to $\alpha\beta$, and consequently the average absorption coefficient at a given frequency is equal to the intensity of the line nearest this frequency divided by $\alpha\beta$. For computational purposes it is convenient to introduce instead of the frequency a quantity x proportional to it; $x=(\nu/\alpha)\sigma^{\frac{1}{2}}$. The contribution to the absorption coefficient made by the zero branch lines may be obtained from I_0 by the transformations indicated,

$$P_0=(L/2\alpha|\beta|)\sigma^{\frac{1}{2}}[(1+\beta)/\pi]^{\frac{1}{2}}e^{-x^2/\beta}\left[e^{-(x/\beta)^2}+(x/\beta)^2\int_\infty^{(x/\beta)^2}u^{-1}e^{-u}du\right].$$

The absorption coefficient is thus given as a function of x, the distance from the center of the band expressed in units of $\sigma^{\frac{1}{2}}/\alpha$. This formula is valid for both the positive and negative values of β.

The remaining lines of the $\perp$ bands correspond to the changes of the quantum numbers $\Delta J=\pm1$, $\Delta K=\pm1$. Taken together they will form a practically continuous region of absorption, which we will designate as background absorption. As before, we shall first treat the intensities exactly, and later approximate them in the region where J and K are large compared with unity.

Consider the background absorption at a point ν frequency units to the high-frequency side of the band center ν_0. The lines which contribute to this absorption may be divided into three classes. First there are the lines where $\Delta K=+1$, $\Delta J=+1$, whose position relative to the center of the band is

$$\nu^{J\ \ K}_{J+1\ K+1}=\alpha(J+1)+\alpha\beta(K+\tfrac{1}{2}),$$

second the lines $\Delta K=-1$, $\Delta J=1$, $\nu=\alpha(J+1)-\alpha\beta(K-\frac{1}{2})$, and third the lines $\Delta K=1$, $\Delta J=-1$, $\nu=-\alpha J+\alpha\beta(K+\frac{1}{2})$. We shall compute the absorption coefficient arising from the first class of lines. The wave-mechanical intensity of a line in this class is

$$I^{J\ \ K}_{J+1\ K+1}=rL[(J+K+2)(J+K+1)/2J]e^{-\sigma J(J+1)-\sigma\beta K^2}.$$

For a given value of K the lines of this class are uniformly spaced in frequency with an interval between them of α. The absorption coefficient is therefore $P=I/\alpha$. There will, however, be contributions to the absorption coefficient at this point from transitions involving various values of J and K in all those cases where the quantum numbers satisfy the relation[4]

$$\nu=\alpha(J+1)+\alpha\beta(K+\tfrac{1}{2}).$$

The total background absorption at the point ν of the class I lines may be found by eliminating J from the above intensity expression and summing over all the allowed values of K, thus

$$(P_b)_1=(rL/2\alpha)\sum_{K=0}^{K=(\nu/\alpha-1-\beta/2)/(1+\beta)}\frac{[\nu/\alpha+1-\beta/(K+\frac{1}{2})][\nu/\alpha-\beta(K+\frac{1}{2})]}{\nu/\alpha-1-\beta(K+\frac{1}{2})}e^{-f(\nu,\,\alpha,\,K)},$$

where

$$f(\nu,\alpha,K)=\sigma\{[\nu/\alpha-\beta(K+\tfrac{1}{2})]^2-(3\nu/\alpha)\beta(K+\tfrac{1}{2})+2+\beta K^2\}.$$

The L in this expression corresponds exactly to the L appearing in the formula for the $\parallel$ bands and is equal to the total intensity of the complete band. We may now proceed to approximate the above expression; as before, we take J and K to be large compared with unity, and replace the summation by an integration:

$$(P_b)_1=(rL/2\alpha)\int_0^{\nu/\alpha(1+\beta)}\{[(\nu/\alpha)+K(1+\beta)]^2/[(\nu/\alpha)-\beta K]\}e^{-\sigma\{[(\nu/\alpha)-\beta K]^2-\beta K\}}dK.$$

The contributions to the absorption coefficient arising from the lines in classes II and III may

[4] Of course, if β is irrational only one set of values of J and K will satisfy this relation, i.e., only one line falls

be treated in a similar manner. The total absorption coefficient, P_b, is then the sum of these three terms. We introduce the variable $x=(\nu/\alpha)\sigma^{\frac{1}{2}}$, together with the following symbols, $B=(1-\beta)/(1+\beta)$; $C=x/[|\beta|(1+\beta)]^{\frac{1}{2}}$ $y=2C|\beta|/(1-\beta)$. For computational purposes three ranges of β must be considered separately, $\beta<0$, $0\leq\beta\leq1$, $\beta>1$.

$\beta<0$,

$$P_b=(L\sigma^{\frac{1}{2}}/2\alpha\pi^{\frac{1}{2}})\beta^{-2}(1+\beta)^{\frac{3}{2}}e^{-x^2/(1+\beta)}\left[B^2(1-e^{y^2})/2+(B^2C-2B)\int_0^y e^{-\nu^2}d\nu+C^2\int_{-y}^0(\nu+c)^{-1}e^{\nu^2}d\nu\right].$$

$0\leq\beta\leq1$,

$$P_b=(L\sigma^{\frac{1}{2}}/2\alpha\pi^{\frac{1}{2}})\beta^{-2}(1+\beta)^{\frac{3}{2}}e^{-x^2/(1+\beta)}\left[B^2(1-e^{-y^2})/2+(B^2C-2B)\int_0^y e^{-\nu^2}d\nu+C^2\int_0^y(\nu+c)^{-1}e^{-\nu^2}d\nu\right].$$

$\beta>1$,

$$P_b=(L\sigma^{\frac{1}{2}}/2\alpha\pi^{\frac{1}{2}})\beta^{-2}(1+\beta)^{\frac{3}{2}}e^{-x^2/(1+\beta)}\left[B^2(1-e^{-y^2})/2+(B^2C-2B)\int_0^{-y}\left[e^{-\nu^2}d\nu\right.\right.$$

$$\left.\left.+C^2\left\{e^{-C^2}\int_{y^2-C^2}^{\infty}u^{-1}e^{-u}du+\int_0^{-y}(\nu+C)^{-1}e^{-\nu^2}d\nu\right\}\right].$$

These expressions may be readily evaluated with the exception of the final definite integrals. Even here the integrands are relatively simple functions and accordingly the values of the integrals may be obtained rather easily by means of numerical quadrature.

The results of these computations have been collected in Fig. 2, which represents the envelopes of the $\perp$ type bands for $\beta=-\frac{1}{2}$, $-\frac{1}{3}$, $\frac{1}{2}$, 1, and 4, respectively.

For each value of β the full line represents the total absorption coefficient (zero branches plus background) as a function of x, while the dotted line gives the absorption coefficient due to the zero branch lines alone. The two vertical lines along the axis indicate the doublet separation of the parallel type band for the same value of β.

For $\beta=-\frac{1}{2}$ the envelope presents the appearance of three almost equal maxima with a doublet spacing considerably smaller than that of the corresponding parallel band. As β grows the central peak becomes sharper and higher, while the doublet spacing increases. At $\beta=0$ we have all three moments of inertia of the molecule equal, and there is no distinction between a $\perp$ and a $\parallel$ type band. For larger values of β the

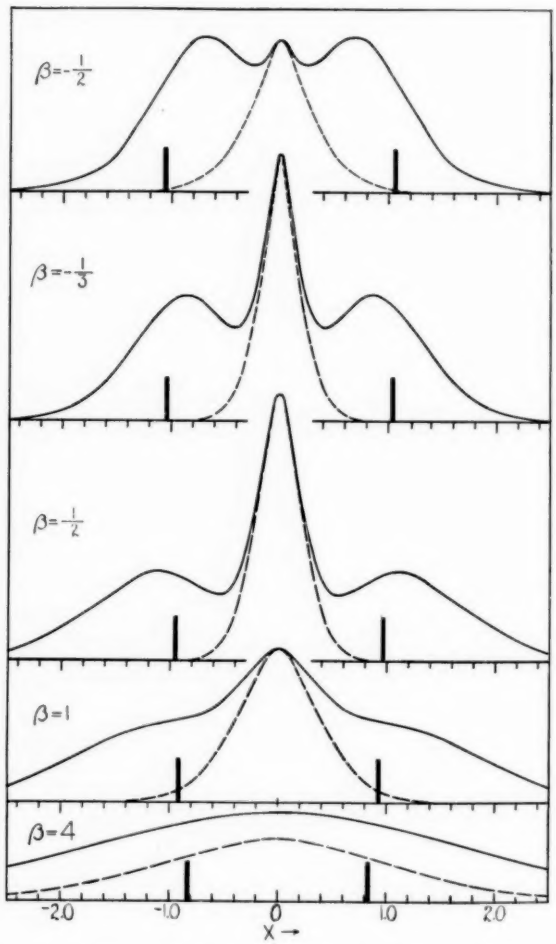

FIG. 2. Envelopes of the $\perp$ type bands for various values of β.

exactly at a given point, ν. We are, however, not interested in the intensity at a point, but rather in the average absorption coefficient in its immediate neighborhood. Thus for any particular K we are interested in the Jth line which most nearly satisfies the frequency relation.

central peak becomes broader and lower, while the doublet separation increases over that of the $\parallel$ type band. For values of β greater than unity the envelope no longer presents the appearance of three maxima, and for sufficiently large values of β the envelope resembles a Gauss error curve. In fact it may be shown that in the limit of large β the total absorption coefficient is given by

$$P=(L/\alpha\beta)\left[\sigma(1+\beta)/\pi\right]^{\frac{1}{2}}e^{-x^2(1+\beta)/\beta^2}.$$

§4. Discussion and Application

Before proceeding to apply the results of the foregoing calculations we shall discuss the region in which they are valid. The intensity formulae for those lines near the center of the band (or their envelope) may well be somewhat in error, because our approximation has been one which implies that K and J are large compared with unity. This limitation is not at all a serious one since the intensities of these lines may be readily computed from the exact formulae (i.e., the summations consist of only a few terms).

A second limitation of a much more serious character affects our formulae for the intensities (or envelopes) of the lines of the perpendicular bands. If the symmetry of the symmetrical rotator is a result of a geometrical symmetry of the atoms forming the molecule the lines of the perpendicular bands may suffer certain anomalies. Thus it is well known that the spacing of the fine structure lines of the infrared bands of methane is not a constant, but varies from band to band. The same phenomenon is observed in the $\perp$ bands of the methyl halides. A theory of this effect based on an interaction between vibration and rotation has been proposed by Teller and Tisza.[5] Their general conclusions may be stated very simply, *viz.*, the position of a line corresponding to the transition $\Delta K=\pm1$, $\Delta J=0$, ±1 will be given by the following expressions respectively

$$\nu=\nu_0\pm\alpha J\pm\alpha(\beta+\beta')(K\pm\tfrac{1}{2});\quad \Delta J=\pm1$$

$$\nu=\nu_0\pm\alpha(\beta+\beta')(K\pm\tfrac{1}{2});\qquad \Delta J=0.$$

As before $\beta=(A/C)-1$ but β', which may be of the same order of magnitude as β, depends upon the anharmonic terms in the potential energy and cannot be evaluated without a more detailed knowledge of the molecular structure than we now possess.

Thus the spacing of the lines in a $\perp$ band of this class of molecule gives no direct information concerning the moments of inertia of the molecule. The envelope of these lines depends directly upon β' and consequently it also cannot be predicted *a priori*. However, Teller and Tisza's theory shows that while the positions of the lines depend upon β', their intensities are just what they would be if β' were zero. Consequently if β' were known the envelope would be given through a simple modification of our expressions. Fortunately this second limitation does not at all apply to the lines of the parallel bands. Although the infrared spectra of a considerable number of molecules of the symmetrical rotator class have been investigated only one group, the methyl halides, has so far yielded data to which our theory may be applied. It is true that in addition to these the spectrum of ammonia has been observed, but the moments of inertia of this molecule are so small that the fine structure lines are relatively few in number and completely separated. It is more suitable in the case of this molecule to use the exact expressions for the intensities of the lines. The spectra of other symmetrical molecules with large moments of inertia have been mapped, but not with spectroscopes of sufficiently high resolving power to reveal the structure of the envelopes. There seems, however, to be no reason why these envelopes cannot eventually be obtained.

The infrared spectra of the methyl halides have been observed by Bennett and Meyer[6] in the region from 3μ to 14μ and by Moorhead[7] in the region from 1.5μ to 3μ. A considerable number of parallel type bands were found by both investigators, but only one, the 9.55μ band of methyl fluoride, was resolved into its fine structure lines. The methods by which the bands were obtained were such that the ratio of intensity of the zero branch to that of the whole band is not given with sufficient accuracy to use in our formulae. The measured values of the

[5] Teller and Tisza, Zeits. f. Physik **73**, 791 (1932).

[6] Bennett and Meyer, Phys. Rev. **32**, 888 (1928).

[7] J. G. Moorhead, Phys. Rev. **39**, 788 (1932).

TABLE I. *Measured values of doublet separation.*

	B. and M.	M.	$\Delta\nu$	$A\times10^{40}$
CH_3F	43, 44	—	43.5	32
CH_3Cl	35, 28, 28, 23	35, 33, 28	30.0	61
CH_3Br	25, 23, 23	26, 25, 24	24.2	89
CH_3I	23, 21, 21	27, 24, 21	22.8	99

doublet separation seem to be fairly concordant and these we have collected in Table I. The first column gives the measurements of Bennett and Meyer and, the second the measurements of Moorhead, while the third column represents their average in waves/cm. These experimental values for the doublet separation are each determined independently since the bands in question lie in quite different regions of the spectrum.

This one datum, the doublet separation, does not serve to determine either A or C but does constitute a relation between them. In the case of the methyl halides we may obtain an additional relation by assuming that the moment of inertia along the symmetry axis C, is the same for each molecule and is equal to the moment of inertia of methane. This assumption seems very plausible and is equivalent to assuming that the methyl group is relatively little influenced by the halide atom. In any case since β is large the value of A as determined from the doublet separation is relatively insensitive to small changes in C.

Teller and Tisza have estimated the moment of inertia of methane to be 5.3×10^{-40}. With this value and the relation between C, β and S mentioned previously, we obtain the values for the moment of inertia A which are given in the fourth column of Table I. No great accuracy can be claimed for these values and it would be very desirable to have a check on them. In the case of methyl fluoride this is possible since the fine structure of one of the bands has been resolved, yielding the value $A=39.5\times10^{-40}$. The agreement is not good but may be regarded as fairly satisfactory.

An estimate of the distance between the carbon and the halide nuclei may be made if we continue to use the assumption that the methyl group is identical in all the methyl halide molecules and is equal to the methyl group in methane. On this basis our values for A and C determine the following distances in Angstroms $C-Cl=1.80$; $C-Br=1.99$; $C-I=2.05$.

The $C-Cl$ distance in methyl chloride has been measured by R. Wierl,[8] from electron diffraction patterns and found to be 1.85 ± 0.06. Our results for the internuclear distances may also be compared with the atomic radii as determined by Pauling.[9] According to Pauling's work $C-Cl=1.76$, $C-Br=1.91$, and $C-I=2.10$.

[8] R. Wierl, Ann. d. Physik **8**, 521 (1931).
[9] L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Aluminum-Magnesium Mirrors

The writer has prepared metallic mirror surfaces which have shown unusually high and uniform coefficients of reflection throughout the visible light. These mirrors were made by evaporation of the metals in a vacuum and were deposited upon glass.

Surfaces made from pure aluminum reflected 89.5 percent of the light, incident at 10°, for each of the three regions of light used. For this purpose white light from a tungsten filament was filtered by using a standard set of the Wratten three color taking filters for tricolor reproduction work. The red filter (A25) transmits a band from approximately 7000 to 5800, the green filter (B58) from 6200 to 4800 and the blue filter (C5–47) from 5200 to 3600. Intensities were measured by a Weston Photronic cell.

Mirrors prepared by evaporating aluminum and magnesium were found to reflect 94 percent in each of the three color regions. Other mirrors were found to reflect 93 percent.

The unusual feature of such surfaces is their high reflection characteristics, particularly in the blue end of the spectrum. Front surfaces of silver, chemically deposited, reflect 95 percent at the red end of the spectrum, while only 85 percent at the blue end. The writer has not yet measured the reflection in the ultraviolet. Since the reflection power of these mirrors is uniform in the visible spectrum, one would expect a good performance in the ultraviolet, perhaps better than any known substance.

Unfortunately the exact composition of the aluminum magnesium surfaces has not yet been obtained with any reliability because of the difficulties involved in making an accurate quantitative analysis. A number of analyses have been made with results varying from 10 to 50 percent for the magnesium. The mass of the films is of the order of one milligram which makes reliable determinations rather difficult. Further experimental work is being conducted with the object of finding the best combination.

The best mirror yet obtained was made by evaporation from the two metals in separate pieces, the mass of the aluminum being 10 times greater than that of the magnesium. This, of course, does not mean that the reflecting surface had a similar composition, for while the melting points of the two metals are nearly identical (Mg 651°C and Al 658°C) the boiling point of magnesium is 1120°C and that of aluminum is 1800°C, hence one would expect the vapor pressure of magnesium to be the larger of the two and that the magnesium would therefore be deposited in a correspondingly larger ratio.

Mirrors made of a proper proportion of aluminum and magnesium should be of considerable value in various optical instruments where front surfaces of high reflecting power are desirable. A further admirable feature of this combination is to be found in the fact that the surface is protected by aluminum oxide which is exceedingly hard and is not as readily tarnished as silver. A detailed study of the preparation and properties of these mirrors is in progress and will be published as soon as it is complete.

HIRAM W. EDWARDS

University of California,
January 9, 1933

Actinouranium and the Geologic Time Scale

From all evidence now available it appears that the actinium series originates in one or more long lived isotopes of uranium, called actinouranium isotopes. The question is, whether one or two such isotopes exist. If there are two, their isotopic weights must be 239 and 235, and the actinium series would presumably be produced by the scheme of disintegration portrayed in Fig. 1. We shall use the subscripts 1, 2, 3, and 4 to designate quantities characteristic of the isotopes U^{238}(U I), U^{234}(U II), U^{239}, and U^{235}, respectively.

Hahn[1] has searched for the hypothetical beta-rayers required by the scheme of Fig 1 and has found no evidence for their existence. His work makes it very probable that there is a single actinouranium isotope, U^{235}, which is the immediate parent of UY. As a working hypothesis, we have assumed that such is the case; and have determined probable values of the decay constant and abundance of this isotope with the aid of existing physical and chemical data.

These data are: the "branching ratio" B of the uranium and actinium series; chemical analyses of certain radioactive minerals; the isotopic composition of the leads from these minerals; isotopic weights of Pb^{206}, Pb^{207}, and Pb^{208}, atomic weights of ordinary lead, and of thorium and uranium; the decay constant of thorium; and the present rate of disintegration of uranium. A critical examination of these data was found necessary. The results of the investigation are as follows.

[1] O. Hahn, Zeits. f. anorg. Chem. **147**, 16 (1925); Zeits. f. angew. Chem. **42**, 927 (1929).

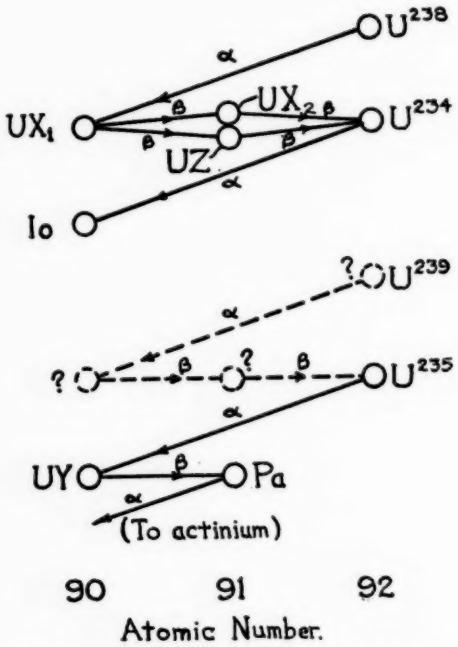

FIG. 1. Connection of the uranium and actinium series.

The hypothesis adopted demands that the "branching ratio" shall be constant at any given time although it varies through the course of geologic time. In a recent note[2] we have recomputed certain published values of the branching ratio, using an equation based on the actinouranium hypothesis. This correction, however, is unimportant, compared with variations between the results of different investigators.[3] Further work will be necessary to determine in detail the causes of these variations. The probable value of the ratio lies between three and four percent.

A thorough examination of the data on the weights of the three principal isotopes of lead gave 205.98 ± 0.03 as the most probable value for Pb^{206}, with those for the other two differing from this by integers. We have also computed the loss of mass in disintegration for the members of the three radioactive series. These data have made it possible to determine the weights of the radioactive isotopes, and the atomic weights of radium, thorium and uranium. The latter do not agree with the present accepted values and are to be preferred to them.[4]

We have obtained rigorous equations, too complex to be presented here, which make it possible to determine the decay constant, λ_4, of the isotope U^{235}. They also afford the means for accurate determinations of the decay constant, λ_1, of U^{238}, and of the ages of certain radioactive minerals. Computations of these quantities have been made for four minerals. Aston[5] has given isotopic analyses of the lead contained in three of these minerals. Two values of the "branching ratio" B (3 and 4 percent, respectively) have been used in each case. Internal evidence indicates that the λ_4-values from the thorite of Brevik, Norway and the kolm of Grüllhögen, Sweden are untrustworthy. On the other hand the mean decay constants obtained from Karlshus bröggerite and Wilberforce uraninite are in fair agreement, and the data are such that they cannot be far from correct, always assuming there is only one actinouranium isotope. The results are given in Table I.

TABLE I.

	$B=0.03$	$B=0.04$
$10^9\,\lambda_4$ in yr.$^{-1}$		
From bröggerite:	2.62	2.07
From uraninite:	1.94	1.51
Mean:	2.28	1.79
$10^9\,\lambda_1$ in yr.$^{-1}$, mean:	0.1514	0.1509
Half life of U^{235} in yr.	3.10×10^8	3.96×10^8
Half life of U^{238} in yr.	4.58×10^9	4.60×10^9

The ages are as follows, in billions of years:

B:	0.03	0.04
Karlshus bröggerite:	0.805	0.809
Wilberforce uraninite:	1.036	1.041

An analysis of the effects of weathering and leaching on the determination of the ages of radioactive minerals has been made. It is found that in cases where most of the alteration occurred recently, in an interval short compared with the life of the mineral, an isotopic analysis, together with the value of the decay constant of U^{235}, would make possible a correct age determination. Equations have been developed to show the effect of uniform leaching. By way of illustration, they are applied to Katanga pitchblende, by using $B=0.03$, with the following results: $\lambda_4=2.83\times10^{-9}$ yr.$^{-1}$; $\lambda_1=0.1514\times10^{-9}$ yr.$^{-1}$; age $=0.55\times10^9$ yr. No statement can be made as to the reliability of these determinations, for several approximations are involved. However, the age thus obtained agrees with that calculated from the lead-uranium ratio, 0.080, for several unleached specimens, using the mean value of λ_4 obtained from the Karlshus bröggerite and the Wilberforce uraninite.

An equation based on the actinouranium hypothesis, for determining the ages of minerals when λ_4 is known, has been given by Kovarik.[6] It takes account of original common lead, and is as follows:

$$e^{\lambda_1 t}-1+0.194\frac{\lambda_1}{\lambda_4}(e^{\lambda_4 t}-1)-0.643\frac{\mathrm{Th}}{\mathrm{U}}\left(1+B\frac{\lambda_1}{\lambda_4}\right)(e^{\lambda_{\mathrm{Th}} t}-1)$$
$$=(207.22-W)\frac{238.04}{W}\frac{\mathrm{Pb}}{\mathrm{U}}\left(1+B\frac{\lambda_1}{\lambda_4}\right).$$

[2] Western and Ruark, Abstract 10, Chicago Meeting of the American Physical Society, Phys. Rev. **42**, 903 (1932).

[3] Wildish, Jour. Amer. Chem. Soc. **52**, 163 (1930); von Grosse, Phys. Rev. **42**, 565 (1932).

[4] Western and Ruark, Abstract 11, Chicago Meeting of the American Physical Physical Society, Phys. Rev. **42**, 903 (1932).

[5] Aston, Nature **129**, 649 (1932).

[6] Kovarik, Amer. Jour. Sci. **20**, 81 (1931).

W is the atomic weight of the lead contained in the mineral, while Pb, Th, and U are the weights of lead, thorium and uranium, respectively, in a given sample. This equation may also be applied to the determination of the "age of the earth's crust" from the amounts of Pb, Th and U in the average igneous rock. In the absence of data on the atomic weight of average rock lead, we have applied this equation to a Vesuvian lava of atomic weight 207.05 which yields an apparent age of 1.5 billion years, both for $B=0.03$, and $B=0.04$. The interpretation of this value is of course very difficult, involving as it does both data on lava and on the average igneous rock.

The hypothesis of two actinium isotopes, U^{239} and U^{235}, has been considered in some detail, although it is considered improbable. If the half lives of both were of the order 5×10^8 years, it is possible they would not have come into equilibrium at the time when old radioactive minerals were formed, say 1 to 1.5 billion years ago. The view is advocated that in such a case it is reasonable to assume that the actinouranium isotopes are in equilibrium *at the present time*, rather than that they were in equilibrium initially. On this basis equations are developed showing the amounts of U^{235} and Pb^{207} which would be present at any time.

FORREST WESTERN
ARTHUR E. RUARK

Department of Physics,
University of Pittsburgh,
January 12, 1933

On a Relativistic Particle with a q-Number Charge

It may be not without interest to consider the possibility of existence of a particle having a charge e, where e is a q-number. Inspection of the γ's used in proving the Lorentz invariance of the Dirac equation[1] leads to the conclusion that the invariance is preserved if e commutes with α_x, α_y and α_z. Also, e can be prevented from being a constant of motion by requiring that it should not commute with α_m. In the special case of four-component wave functions these conditions can be satisfied in only one way, namely by letting

$$e=e_0+e_1\rho_1, \tag{1}$$

where e_0 and e_1 are c-numbers.

Professor G. Breit pointed out to the writer that the terms in the Hamiltonian due to $e_1\rho_1$ in (1) are associated with a known covariant.[2]

The question whether or not the various quantum-mechanical expressions which result when e is allowed to be a q-number can be given a satisfactory physical meaning is being studied.

V. ROJANSKY

Union College,
Schenectady, New York,
January 18, 1933

[1] P. A. M. Dirac, *The Principles of Quantum Mechanics*, Chapter XIII, Oxford, 1930.

[2] G. E. Uhlenbeck and O. Laporte, Phys. Rev. **37**, 1552 (1931); k_m in Eq. (8).

The Index of Refraction of Water and Its Thermal History

By the use of a sensitive differential method, A. P. Wills and G. F. Boeker (Phys. Rev. **42**, 687 (1932)), report measurements which indicate that the diamagnetic susceptibility of water depends upon the thermal history of the sample. They suggest that the establishment of equilibrium between the polymers of water may require a considerable time (at least five hours) after changing the temperature.

Although it is generally accepted that the association equilibria are established with great rapidity, yet it is possible that the methods previously employed in reaching this conclusion are not sufficiently sensitive to detect time lags in the equilibrium. For example, Menzies,[1] records negative results for vapor pressure measurements sensitive to ±0.05 mm Hg on recently frozen water. On the other hand, H. T. and T. C. Barnes[2] claim that water from recently condensed steam contains less of the physiological active polymer trihydrol and affects the growth of spirogyra in a quite different way from water (presumably) enriched with the trihydrol modification by freezing. Recently Brüll[3] has reported that the freezing point and specific volumes of carbon tetrachloride depend upon the rapidity with which the liquid has been chilled from $+40°$ to $-20°$C.

Since the index of refraction should presumably parallel diamagnetic susceptibility and since the former can be measured with very high precision ($\pm3\times10^{-6}$ using 4 cm cells) with the Haber-Löwe-Zeiss instrument at our disposal we have compared the indices of distilled water boiled three hours and rapidly chilled (within five minutes), with that of water similarly treated but which had aged for three days. No difference in index of refraction was noted over a period of forty-four hours, except in a preliminary experiment which was later shown to be due to a leak in the cell. Readings could be taken about one-half hour after the cooling, this time being necessary to obtain the temperature equilibrium in the instrument necessary for precise matching of the bands.

Since minute traces (of the order of 10^{-6} mols/liter) of hydrogen or hydroxyl ions will markedly catalyze rearrangements like the keto-enol transformations, it is possible that our negative results might be due to traces of acid or alkali arising from exposure of the water to the atmosphere or to glass. Special precautions were accordingly taken in the later experiments to exclude as far

[1] Menzies, Proc. Nat. Acad. Sci. **18**, 567 (1932).

[2] H. T. and T. C. Barnes, Nature **129**, 691 (1932); Proc. Nat. Acad. Sci. **18**, 136 (1932).

[3] Brüll, Zeits. f. Electrochemie **38**, 601 (1932).

as possible contact with glass and carbon dioxide. A current of carbon dioxide-free air was passed through distilled water at room temperature and then for one hour just below the boiling point. The water was then redistilled with a quartz still in a current of carbon dioxide-free air directly into the metal interferometer cell, of which only the windows necessary for the optical path were made of glass. This preparation when compared in the interferometer with equilibrium water, showed no detectable variation in index of refraction over a period of twenty hours.

VICTOR K. LA MER
M. L. MILLER

Department of Chemistry,
Columbia University,
January, 23 (1933)

The Recombination of Atomic Hydrogen.[1, 2]

A recent publication dealing with the kinetics of the recombination of hydrogen atoms[3] states that hydrogen molecules are almost exclusively effective as third bodies in the triple collisions necessary for recombination, the effect of hydrogen atoms as third bodies being too small to be detected (less than ten percent). Their contention is supported by the fact that the reaction velocity constants for the reaction of two hydrogen atoms in the presence of a hydrogen molecule as a third body do not vary with time or pressure whereas the constants for the reaction of two hydrogen atoms with both hydrogen molecules and hydrogen atoms regarded as equally efficient third bodies, show definite drifts. Due to a serious error in the derivation of the expressions for the velocity constants, however, their conclusions are erroneous.

If we consider a mixture of atomic and molecular hydrogen flowing through a tube, we find a time decrease in the number of hydrogen atoms at a given point x, due to the streaming of the gas. This may be represented by the equation of continuity, namely $-(\partial \mathrm{H}/\partial t)_x = \partial(v_x \mathrm{H})/\partial x$, where V_x, the linear velocity of the gas stream *at the point* x, is given by $v_x = n_0/[\pi r^2(\mathrm{H}_2 + \frac{1}{2}\mathrm{H})]$ where n_0, in molecules per second, is the quantity of molecular hydrogen admitted to the apparatus and r, the radius of the tube. The concentration of molecules and atoms at the point x in molecules per cc is given by

$$\mathrm{H}_2 = \frac{P}{kT}\frac{1-\alpha}{1+\alpha} \qquad \mathrm{H} = \frac{P}{kT}\frac{2\alpha}{1+\alpha}$$

where α is the degree of dissociation of molecular hydrogen and P the pressure, in dynes/cm², at the point in question. Making the substitution we obtain

$$v_x = \frac{n_0 kT(1+\alpha)}{\pi r^2 P}.$$

Steiner and Wicke state that the pressure in the recombination tube can be regarded as constant during a single run, since the pressure difference at the ends of the tube is but ten percent of the total. Yet they use a constant value for the linear velocity of the gas stream and incorrectly write the equation of continuity $-(\partial \mathrm{H}/\partial t)_x = v_x(\partial \mathrm{H}/\partial x)$. In one set of experiments, for example, α varied from 0.55 to 0.25 so that the linear velocities at the ends of the tube would be in the ratio 1.55/1.25 if we assume that the pressure does not vary. If we include the ten percent pressure drop, the values of v_x become more constant but the values of the reaction velocity constants still differ materially from those obtained by Steiner and Wicke since the pressure occurs cubed in the expressions for these rate constants. Unfortunately, the authors do not give sufficient data to enable one to correctly calculate reaction velocity constants from their experimental data, but it is at once obvious that the agreement between the values of the constants for the combination of two hydrogen atoms in the presence of a hydrogen molecule, disappears when the variation of pressure and linear velocity is taken into account. It appears, therefore, that Steiner and Wicke have not established the exclusive efficiency of the hydrogen molecule as a third body and that their results cannot be considered as contradictory to those of Smallwood[4] and Amdur and Robinson[5] who find that hydrogen atoms and hydrogen molecules have approximately the same efficiencies as third bodies.

I. AMDUR

Research Laboratory of Physical Chemistry,
Massachusetts Institute of Technology,
January 23, 1933

[1] National Research Fellow in Chemistry.

[2] Contribution No. 301.

[3] Steiner and Wicke, Zeits. f. physik. Chemie, Bodenstein-Festband, 817 (1931).

[4] Smallwood, J. Am. Chem. Soc. **51**, 1985 (1929).

[5] Amdur and Robinson, in press.

Atomic Disintegration by a Relatively Slow Neutron

A photograph (shown at the November meeting) of the disintegration of an atom, presumably nitrogen, by the capture of a neutron of lower velocity than any found to be effective in the work of Feather, was obtained several months ago (Fig. 1). Beryllium powder was mixed with a radiothorium salt and this mixture was used as the source of neutrons. Fig. 2 gives the angles and ranges of the particles, and Table I, their velocities. Only one similar set of values has been published (Feather, Proc. Roy. Soc. **A136**, 719 (1932)).

In the present collision, kinetic energy was very nearly conserved, and so any γ-radiation emitted, or energy stored up in an unstable atom, comes mostly from the loss of mass which occurs. The decrease of mass was calculated on the basis of the value 1.0067 ($O^{16} = 16.0000$) for the neutron. The mass of the neutron must be greater than

1.0057 if there is any decrease of mass in the formation of the H^2 nucleus from a proton and a neutron.

FIG. 1

TABLE I.

$N^{14}+n^1 \rightarrow B^{11}+He^4$

Ranges in air at 760 mm and 15°C:	He : 8.5$_6$ mm		
	B : 1.57 mm		
Nuclear masses $O^{16}=16.0000$	N : 14.008		
	n : 1.0067		
	B : 11.011		
	He : 4.00216		
Calculated momenta perpendicular to path of neutron: g·cm/sec. $\times 10^{15}$	B : 4.62	4.62	
	He : 4.44	(4.62)*	
Velocities: cm/sec. $\times 10^{-8}$	B : 2.55	2.55	
	He : 8.54	8.87	
	n : 19.07	19.89	
Kinetic energies: electron-volts $\times 10^{-6}$	B : 0.371	0.371	
	He : 1.513	1.634	
	n : 1.898	2.065	
Loss of kinetic energy for the disintegration: electron-volts $\times 10^{-6}$		0.014	0.060
Loss of mass for the disintegration:	mass units.....		0.0015
	electron-volts $\times 10^{-6}$.....		1.40

* The range of the helium nucleus produced by the disintegration could not be measured with the same accuracy as the range of the boron nucleus, since the end of the helium track was broad and faint. The values given in the second column were therefore calculated, attributing to the helium nucleus the same momentum perpendicular to the path of the neutron as was found for the boron nucleus in the opposite direction.

While it is true that radiothorium gives slower as well as faster α-particles than polonium, yet the α-particles from any source are slowed down by passage through the beryllium, so that it is remarkable that all of the neutrons effective in producing disintegrations have had velocities corresponding to more than 1.9 million electron-volts. Since the neutron has an excess mass, of the order of

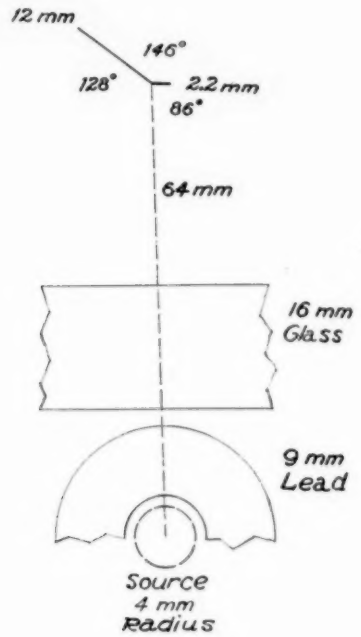

FIG. 2

0.006 unit, which may be utilized in the disintegration of atoms with which it unites, this probably means that not many lower velocity neutrons from beryllium are present, especially since protons with only about 0.007 or 0.008 unit of excess mass prove effective at velocities of the order of 10^5 electron-volts.

WILLIAM D. HARKINS
DAVID M. GANS
HENRY W. NEWSON

George Herbert Jones Laboratory,
University of Chicago,
January 10, 1933.

PROCEEDINGS

of the

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE PASADENA MEETING, DECEMBER 16–17, 1932

The 181st meeting of the American Physical Society was held in the lecture hall, room 201, of the Norman Bridge Laboratory of Physics of the California Institute of Technology on Friday, December 16th and the morning of Saturday, December 17th. There were three sessions. The morning sessions began at 9:30 and the afternoon sessions at 2:00. The meetings were presided over by Professors R. A. Millikan and Richard C. Tolman with some hundred members in attendance. The members of the society were tendered a luncheon at the Atheneum on Friday by the Institute and met at an informal dinner Friday evening. It was voted to hold the 185th meeting on the Pacific Coast in affiliation with the meetings of the Pacific Division of the A.A.A.S. at Salt Lake City on Thursday, June 15th and Friday June 16, 1933. This program will allow for the giving of papers on a ten minute program basis and will leave time enough for members so desiring to arrive in Chicago in time for the Physical Society program at the Century of Progress Exposition. At the dinner on Friday evening an informal discussion was held concerning the formation of local Physical Society Sections in analogy to the Section recently organized in New England. Representatives from the leading Pacific Coast Institutions excepting those in the State of Washington were present. The Secretary gave a summary of the replies he had received from the various institutions on the coast from whom he had received written statements including the Washington group. It appeared from the discussion that the geographical distances involved on the coast between the various physical centers and the close informal contacts already existing between neighboring institutions in any locality rendered any section organizations on the coast (such as Northwestern Pacific, or California sections) futile and unnecessary. The group expressed itself as unanimously in favor of the present informal organization for the administration of meetings and with the nationalized character of the present meetings on the coast and went on record as in favor of the continuation of the present system.

The abstracts of the papers presented are given below.

LEONARD B. LOEB,
Local Secretary for the Pacific Coast

ABSTRACTS

1. New method of measuring electric and magnetic properties of metals in the region of ultra-short electromagnetic waves. G. POTAPENKO AND R. SANGER, *California Institute of Technology.*—In a Lecher system, which consists of two parallel wires and two connecting bridges, the distance between the bridges in the case of resonance does not correspond exactly to the half wave-length. It is always shorter than the half wave-length, the difference being called Bridge contraction (Brückenverkürzung) by Drude. Its value depends upon the reflecting power of the bridges used and this is affected by the self-induction of the bridges (Drude's theory) and by the resistance of the bridges (exact theory). A plate, the size of which is at least of the order of half of the wave-length, is used as one bridge (the plate-bridge, perfectly reflecting). The other bridge consists of wires of different materials and of different diameters (the wire-bridge, poor reflection). Resonance studies make it possible to measure the bridge contraction and the damping of the Lecher system for all kinds of wire used. A theory of the propagation of the waves along the wires of a Lecher system, taking into account the perceptible resistance of the bridge, is developed. This makes it possible to calculate the values of the resistance of the wire-bridge from the measurement of the bridge contraction and of the damping of the Lecher system. Hence, taking into account the skin-effect and comparing the results for nonmagnetic bridges

with those for magnetic bridges, or the results for bridges of different diameters, the electric conductivity and the magnetic susceptibility of the metals of the wire-bridges can be evaluated. The proposed method is checked by preliminary measurements on copper and iron bridges by the use of undamped waves in the region of wave-lengths from 10 to 100 cm.

2. A sensitive stellar photometer. SINCLAIR SMITH, *Mount Wilson Observatory.*—A very sensitive stellar photometer consisting of a photoelectric cell attached to a Hoffmann electrometer has been installed at the Coudé focus of the sixty-inch telescope. The photo-cell is mounted on a short length of brass tubing which in turn is mounted on the electrometer in such a way that the space surrounding the anode extension of the cell can be evacuated. When this space and the electrometer case are evacuated, both surface leakage over the quartz insulation and the effect of stray ions in the air are eliminated. The excellent quartz cells made by Dr. Kunz of the University of Illinois are used in this photometer as the extremely small dark current of these cells allows one to use the full sensitivity of the Hoffmann electrometer. Photo-currents down to 30 electrons per second have been measured with this instrument, but routine work has been confined to stars brighter than the 14th magnitude which release approximately 500 photoelectrons per second. On stars fainter than the 14th magnitude, natural fluctuations in the primary response (i.e., the number of photoelectrons emitted per second) which of course set a limit to the sensitivity of all photoelectric devices, become prominent, so that it becomes necessary to use observing times which are unduly long for routine work.

3. Determination of e/m for an electron by a new deflection method. FRANK G. DUNNINGTON, *University of California.*—To fill the need of a new deflection determination and to provide a more accurate value, a new deflection measurement of e/m is being made. The method used was conceived by Professor Ernest O. Lawrence. The essential points of the method are: Acceleration of electrons to a continuous range of velocities by a radiofrequency electrostatic field, choice of a particular velocity by magnetic field resolution, measurement of this velocity through radiofrequency fields applied to a pair of accelerating slits and a pair of decelerating slits. A most important advantage of this method is that no acceleration voltage need be measured. This, combined with other properties of the method, practically eliminates errors due to contact potentials. Another advantage is the very high observational precision the method makes possible. The present results, although still preliminary, are of an accuracy comparable with published values. The value obtained from two groups of observations made at different electron velocities and with the calculated probable error is $e/m_0=(1.7592\pm0.0006)\times10^7$ e.m.u. The major part of this probable error is due to allowance for possible errors in the magnetic field measurement. However, to allow for still other possible errors the present results may be stated as $e/m_0=(1.7592\pm0.0015)\times10^7$ e.m.u.

4. The value of e/m. RAYMOND T. BIRGE, *University of California.*—Dunnington's value of $e/m=1.7592\pm0.0015$, from magnetic deflection of free electrons, removes the last apparent discrepancy between the results of various methods. Further recent results, of comparable accuracy, are (1) Perry and Chaffee, 1.761 ± 0.001, from electric acceleration of free electrons, (2) Kirchner (weighted average of two results) 1.7587 ± 0.0009 from the same method, (3) Campbell and Houston, 1.7579 ± 0.0025 from Zeeman effect. The weighted average of these four results is 1.75953 ±0.00059 from internal consistency, and ±0.00044 from external consistency. The four results are thus quite consistent with one another. Assuming them to be of *equal* accuracy, one obtains the unweighted average 1.75920 ± 0.00044. Hence 1.759 ± 0.001 appears to be a conservative estimate of the present best direct determination of e/m. Combining this with all available data on e and h (i.e., the writer's solution *l* of Phys. Rev. **40**, 319 (1932) but with a numerical error corrected), one obtains $h=(6.5420\pm0.0083)\times10^{-27}$ erg·sec., $e=(4.7668\pm0.0038)\times10^{-10}$ *e.s* units. $e/m=(1.7592\pm0.0011)\times10^7$ *e.m* units, $1/\alpha=137.374\pm0.048$, as the present most probable values of these constants.

5. The sun and cosmic rays. ROBERT A. MILLIKAN AND H. VICTOR NEHER, *California Institute of Technology.*—New experiments with instruments of increased sensitiveness have been made both at low and at high altitudes. These reveal no trace of a direct solar influence. If any such influence exists it is shown to be so minute in comparison with the indirect influences which produce changes in the atmospheric blanket as to be negligible in comparison.

6. The elastic scattering of electrons by mercury atoms. EDWARD B. JORDAN AND ROBERT B. BRODE, *University of California.*—The angular distribution of electrons scattered elastically by single mercury atoms was studied for electrons of 10 to 800 volts energy and in angle range of 5° to 172°. The values of the atomic scattering coefficient, P_θ, the number of electrons scattered per atom, per unit electron current density, per unit solid angle at an angle θ to the original beam, were calculated from the observed data. The measurements of previous observers were checked in the region from 5° to 120° and new maxima were observed in the region between 120° and 172°. The value of P_θ was found to rise to a relatively large maximum at or near 180° for most of the velocities studied.

7. Direct fusion method for determining the radium content of rocks. ROBLEY D. EVANS, *National Research Fellow. University of California.*—New principles for removing radon from rocks and for measuring minute quantities of radon are presented. Powdered rock specimens are boiled without flux by direct heating in a vacuum, graphite, resistance furnace. The duration of heating is 2½ minutes, which is to be compared with one hour for the quickest of former methods. The gases from the melt are led through an electrostatic ion-trap to the ionization chamber. A small insulation drying device in the ionization chamber protects the amber from water vapor. The natural observational

limit for measurements of small quantities of radon is defined as the point at which the average ionization from the radon just equals the probable statistical variation in the background ionization due to cosmic and local radiation, and an apparatus is described which permits measuring radon down to this limit. A string electrometer measures only the difference in ionization in two identical ionization chambers, both of which contain the same background gases, but only one of which contains the radon to be measured. A systematic study of the percentage of the total radon removed from biotite granite as a function of (a) temperature, (b) duration of heating, (c) fineness of sample grains, showed that temperature is the only important factor, and that 1800°C effects complete radon removal.

8. Portable roentgenmeter. CHARLES C. LAURITSEN, *California Institute of Technology.*—In work with high-potential discharge tubes or other powerful sources of short wave radiation it is of the utmost importance to have exact knowledge of the amount of radiation to which the worker is exposed. This can be obtained most accurately by means of an *r*-meter carried by the person at all times. A convenient form of such an instrument is described. It consists of a small ionization chamber, electroscope and microscope mounted within an aluminum housing of the general size and shape of a fountain pen. The electroscope consists of a gold-coated quartz fiber of diameter 3μ and length 3 mm, one end of which is secured to a fine supporting wire. The instrument in this form is designed to give full scale deflection on the eyepiece scale for 0.1 roentgen, and this is considered to be the maximum permissible daily exposure. For the purpose of measuring the intensity of strong x-ray beams an instrument is used in which the electrostatic capacity is increased by means of one or more concentric tubes inserted in the ionization chamber to form a condenser.

9. A high-potential porcelain x-ray tube. RICHARD CRANE AND C. C. LAURITSEN, *California Institute of Technology.* An x-ray tube which operates successfully up to 650,000 volts has been constructed from a conical porcelain transformer bushing, rated at 750,000 volts external flashover. The porcelain is 5.5 ft. long and 18 inches inside diameter at the large end, and the whole tube is 9 ft. long. Although the bushing had previously been filled with transformer oil, no difficulties were encountered in outgassing the surfaces. With a pumping system of about 300 liters per second capacity, a vacuum of 10^{-5} mm can be maintained, and this does not change appreciably during operation. Cold emission from the anode, rather than gas current, limits the voltage which can be applied. Filament emission currents up to 4 milliamperes can be employed without undue heating of the target. For a given voltage, a porcelain tube of this type is much more compact than a glass tube, the strength of its walls against puncture makes elaborate internal shielding unnecessary, and there is no more difficulty in maintaining a good vacuum than in a glass tube of comparable volume. The source of high potential is the 1,000,000 volt transformer set in the High Tension Laboratory.

10. Secondary electron emission from tantalum. C. L. UTTERBACK AND E. ALLAN WILLIAMS, *University of Washington.*—The electron emission from tantalum was measured when the metal was bombarded with lithium ions. The source of the ions was $(Li_2O)(Al_2O_3)4SiO_3$ which, according to Hundley, (Phys. Rev. **30**, 864 (1922)), yields the isotope $(Li^7)^+$. The metal was cleaned with acid, well outgassed and the system washed out with oxygen. The system was then filled with oxygen at atmospheric pressure, allowed to stand for some time, and then evacuated. Without further outgassing the target, the electron emission and its percentage of the positive ion current was about one half of its value when the target had been given a similar treatment with air. With an outgassed target the emission was much lower than when it contained either air or oxygen. The value of the positive ion currents was of the order of 6×10^{-10} amperes, and the electron current 2×10^{-10} amperes. In all cases, the percent emission was a linear function of the accelerating potential. The potentials from 400 to 1400 volts were used. As tantalum absorbs considerable oxygen, it is possible, that, on impact of the high-velocity lithium ions, unstable compounds are formed which affect the emission. The effect of oxygen is similar to the effect of this gas on thermionic emission of tantalum, as found by Langmuir, (Phys. Rev. **2**, 450 (1913)).

11. The production of 4,800,000 volt hydrogen ions. M. STANLEY LIVINGSTON AND ERNEST O. LAWRENCE, *University of California.*—Improvements in the method recently described (E. O. Lawrence and M. S. Livingston, Phys. Rev. **40**, 19 (1932)) for the multiple acceleration of ions to high speeds have resulted in much higher energies. The method involves the resonance of ions with an oscillating electric field in a magnetic field. Enlargements in the physical size of the apparatus have led recently to the production of hydrogen ions of 3,600,000 volts energy (M. S. Livingston, Phys. Rev. **42**, 441 (1932)). Now by using two insulated electrodes instead of one the capacity in the oscillating circuit is reduced to half. This makes it possible to use shorter wave-lengths and larger magnetic fields for the resonance condition. With oscillations of 22.4 meters wave-length and a magnetic field of 17,550 gauss hydrogen molecular ions have been obtained with energies equivalent to 4,800,000 volt electrons. For nuclear disintegration studies, for which these ions are intended, this is equivalent to 2,400,000 volt protons. At 3,000,000 volts intensities of the order of 10^{-9} amps. are obtained and can certainly be increased. It appears probable that this intensity can also be obtained at the higher energies.

12. High-velocity mercury ions. WESLEY M. COATES AND DAVID H. SLOAN, *University of California.*—The method of successive acceleration of mercury ions previously described by Sloan and Lawrence which gave particles of 1,250,000 electron-volts energy has been further devoloped so as to produce particles of 2,850,000 electron-volts energy. The resistance and the capacity of the accelerator system have been reduced so as to make possible increased efficiency and increased frequency of oscillation. The diameter of the accelerator tubes was considerably decreased

without appreciably diminishing the intensity of the final beam, probably due to the focussing action previously noted. The number of accelerators was increased from 30 to 36 making their combined length 185 cm. The lowest wave-length used was 27.3 meters; the highest voltage applied was 70,000; the greatest step-up ratio used on the oscillator inductance was eight to one. Still higher velocity ions are believed to be attainable with the present tube. Preliminary measurements have shown that each ion upon striking a molybdenum plate produces from seven to ten secondary electrons, with energies of less than 30 volts. Some evidence that a fairly large fraction of the high velocity-ions themselves are scattered from the molybdenum plate has been obtained. Further measurements will be necessary to test this possibility.

13. High-voltage vacuum tube. DAVID H. SLOAN, *University of California.*—A 50 meter wave-length Tesla coil is mounted in an evacuated metal chamber and driven by a 70 kw vacuum tube oscillator. The water-cooled coil is supported only at its grounded end, and is entirely free from insulation; hence there is nothing to break down in the vacuum of 10^{-6} mm of Hg pressure. The free high-voltage end of the coil is intended to support a hollow cylindrical electrode for accelerating ions into one end and out the other a half cycle later, effectively accelerating the ions to double the voltage of the coil. For the production of high-voltage x-rays, an x-ray anode has been used on the free end of the coil (instead of the accelerating cylinder) together with a filament and biasing grid arrangement that gives emission only when the voltage on the anode is in the neighborhood of peak values, resulting therefore in the production of effectively high-voltage d.c. x-rays. Absorption curves indicated 600,000 volt radiation with 5 milliamperes emission. The intensity of the radiation filtered by one-half inch of steel at 50 cm from a copper target was about one roentgen unit per minute per milliampere.

14. The effect of temperature on the reflection of x-rays from bismuth crystals. A. GOETZ AND R. B. JACOBS, *California Institute of Technology.*—Previous experiments by Goetz and Hergenrother on the influence of temperature on the reflectivity of bismuth crystals for x-rays have been continued with higher accuracy. It has been found that the Debye-Waller relation for the temperature effect does not hold and that the deviation from it cannot be ascribed in any simple manner to the occurrence of anharmonics of higher orders at high temperatures which should be expressed as well in the temperature coefficient of the thermal expansion. The existence of a thermal hysteresis for the integrated as well as the maximum reflection for Bi (111) Mo $K\alpha$ was found and thus the existence of a two-phase system within a crystal (amophorous and ideal crystal phase) as has been suggested previously seems to find support.

15. Magnetostriction in bismuth single crystals. A. WOLF AND A. GOETZ, *California Institute of Technology.*—The magnetostriction of bismuth single crystals has been measured in the longitudinal field of a solenoid at approximately 20,000 gauss in two different directions to the principal axis [111] of the crystal. The observations were made in stationary field conditions which renders the experiments isothermal in contradistinction to the adiabatic method of Kapitza. The crystals of pure Bi gave as moduli of magnetostriction (defined by $\Delta l/l = H^2/2\times m_s)m_{s\,||}$ $= +5.7\times10^{-16}$ and $m_{s\perp} = -7.0\times10^{-16}$; i.e., the dilatation occurs parallel to [111] and a contraction normal to [111] measured in the direction of the field lines. These values support Kapitza's recent measurements quantitively fairly well. Furthermore, the influence of foreign atoms imbedded in the crystal was checked and the effects found have been compared with the known influences on crystal diamagnetism: For impurities with one valency less than bismuth (Pb, Sn) a decrease of $m_{s\perp}$ was found which caused the effect to disappear ($m_{s\perp}=0$) at concentrations of 0.45 percent for Sn and 1.9 percent for Pb. For larger concentrations the effect changes its sign into a dilatation in which finally the values are almost twice as large as the original ones. The atomic influence on the magnetostriction reaches 0 in the neighborhood of concentrations close to the solubility limit of the admixture in bismuth. Similar but more complex effects were found for $m_{s||}$. Electronegative impurities (Te) have influences similar to the previous reported effects of electronegative admixtures on crystal-diamagnetism.

16. The thermal expansion of Bi single crystals. T. L. HO AND A. GOETZ, *California Institute of Technology.*—The thermal expansion of Bi crystals with known admixtures of electronegative and electropositive impurities in small concentrations has been determined between room temperature and melting point. The decline of the expansion coefficient before the melting point as reported previously by Roberts and by the authors could be verified; it was found furthermore that admixtures cause definite changes in the thermal expansion at temperatures characteristic for the impurity present, which is interpreted by the influence such admixtures have on the habitus of the mosaic structure of these crystals.

17. Theory of the inverse first power electrostatic field. GEORGE C. MUNRO, *California Institute of Technology.*—The theory of the motion of an ion in an inverse first power electrostatic field resulting from a cylindrical section condenser has been studied under the particular set of conditions where all ions regardless of their energy enter the condenser normal to its leading edge and at the median position in the gap. Taylor series expressions have been obtained which give the exit position, the square of the exit velocity, and the tangent of the angle which the path of any ion beyond the electrostatic field makes with the corresponding line for the ion which travels in a true circle inside the gap. These expressions involve the charge and initial energy of the ion and the constants of the condenser. The existence and location of a virtual point source has been established for this system under the above conditions of collimation. It is intended that this system shall constitute the energy analyzer in the design of a modified Aston type mass-spectrograph. The results of this work will be published in some detail as soon as some acceptable results are

obtained from the spectrograph to be constructed in the near future.

18. The attainment of high vacua in large metal chambers. M. STANLEY LIVINGSTON, *University of California.*—In the development of an apparatus for the production of high-speed hydrogen ions (reported in a preceding abstract) a large metal chamber was used which could not be outgassed and was sealed with wax. The method necessitated a vacuum in which the mean free path was several hundred meters. A very high-speed pumping system was obviously necessary. Although high-speed mercury or oil diffusion pumps are now available, liquid air traps of corresponding speeds are difficult to construct. In the system reported here steel mercury diffusion pumps with a speed of approximately 25 liters/sec. were used, a Megavac furnishing the rough vacuum. Two liquid air traps in series, each fast but relatively inefficient were used, and a third exposed a liquid air cooled surface in the chamber itself. The overall speed of the pumping system was calculated to be 6 liters/sec. Pressures of below 5×10^{-7} mm of Hg were regularly obtained after 6 hours pumping and after 12 hours pumping a pressure of 1×10^{-7} mm of Hg was observed. These pressures were read on an ionization gauge of the standard type calibrated against a calibrated McLeod gauge.

19. Some new coincidence measurements on the cosmic radiation. B. SPARKS AND W. PICKERING. *California Institute of Technology.*—A new vacuum tube circuit has been developed for recording coincidences of two or more Geiger counters. The circuit includes the use of the Thyratron tubes, and has considerable advantages in regards to the elimination of accidental coincidences. Preliminary experiments with inert-gas filled Geiger counters will be briefly discussed. Results of experiments now in progress to determine whether absorption of the cosmic radiation by the sun or moon can be observed, will be reported upon. The authors hope to demonstrate the apparatus in continuous operation during the period of the meeting.

20. An electric-furnace ionization effect. ARTHUR S. KING, *Mount Wilson Observatory.*—If a substance whose ionization potential is not too high is vaporized in the carbon-tube furnace, a temperature may be found which gives, providing abundant vapor is present, practically the whole neutral spectrum and the stronger lines of the ionized atom. A subsequent run of the furnace at the same temperature and total pressure, but with very little of the substance present, shows a spectrum in which the enhanced lines are relatively strong, or better interpreted, in which the neutral spectrum has faded. The neutral lines arising from high levels have disappeared, and those of low level are less persistent than the low-level enhanced lines. This effect, when examined under controlled conditions, was very distinct for the elements tested, these being calcium, strontium, barium, and neodymium. The phenomenon, which has several illustrations in astrophysics, may be explained as the result of conditions in which ionization is taking place freely, but recombination, on account of the few atoms present, is relatively infrequent. As a result of the reduced supply of neutral atoms, the more difficult transitions producing the high-level lines rarely take place. The low-level lines, both neutral and ionized, remain, and at the limit the spectrum should consist of enhanced lines only, though the excitation is a moderate one.

21. The spectra of the calcium I-like ions: manganese VI, iron VII, cobalt VIII, and nickel IX. WILLOUGHBY M. CADY, *Harvard University and California Institute of Technology.*—The spectra of four new ions have been added to the sequence of spectra isoelectronic with Ca I. A vacuum spark produced the radiation, which was analyzed in a vacuum spectrograph with a concave grating set for grazing incidence. The transitions observed were those between the ground configuration, $3d^2$, and the lowest configuration that combines with it, $3d\,4p$. Nearly all the levels to be expected in these configurations were found, for all four spectra. Almost all the allowed transitions among the observed levels were identified, as were several intercombinations and other forbidden lines. Slater's theory for the levels (neglecting fine-structure) in a configuration gives a good fit with the observed multiplets, especially in $3d\,4p$, which is remote from other odd configurations. In $3d^2$, $^1D_2$ is evidently perturbed by $3d\,4s\,^{1,3}D$.

22. Zeeman effect in crystals. F. H. SPEDDING, *University of California.*—The transverse Zeeman effect on the absorption lines of $GdCl_3\cdot6H_2O$ has been photographed at various field strengths and at several temperatures of the crystal. Slides of the patterns obtained and of typical microphotometer curves will be shown. The results are explained on the assumption that if an electron is excited, as a first approximation, only its spin can orient in a magnetic field.

23. The auroral spectrum. JOSEPH KAPLAN, *University of California at Los Angeles.*—The first negative bands of nitrogen, which comprise most of the nitrogen radiation in the auroral spectrum, have been excited under conditions which suggest those in the aurora very closely. Active nitrogen is produced in uncondensed discharges in concentrations sufficient to give a strong visible glow. A very strong flash is observed at the beginning of the afterglow, and this flash indicates a high concentration of active material in the exciting discharge itself. Under the best conditions for the production of the afterglow the spectrum of the exciting discharge consists almost entirely of the first negative bands. The most important characteristic of these bands, as excited under the present conditions, is the absence of lines due to N^+. The usual excitation of the N_2^+ bands in discharges at low pressures produces these lines, whereas they are almost entirely absent in the auroral spectrum The excitation of N_2^+ bands in the present experiments is thought to be due to the large concentration of metastable nitrogen molecules in the $A\,^3\Sigma$ state, and this experiment is presented as a proof of their presence in both the aurora and in nitrogen afterglows.

24. The extreme ultraviolet spectrum of molecular hydrogen. C. RULON JEPPESEN, *University of California.*—

The spectrum of hydrogen in the extreme ultraviolet has been photographed by means of a new grazing incidence spectrograph containing a two meter grating. More than 2200 lines between 810A and 1375A have been measured. Of these over 1400 are new. The $2p^1\Sigma - 1s^1\Sigma(B-A)$ band system has been extended so that a number of bands ending on the three lowest vibrational levels are now included. The new data on the two lowest vibrational levels agree well with the published Raman effect data. A new analysis of the $2p^1\Pi cd - 1s^1\Sigma(C-A)$ system has given more accurate values of the constants of the $2p^1\Pi cd$ state and has brought to light a number of perturbations. Rotational and vibrational constants for all observed levels in the three above named states have been derived, and tables of the value of the rotational energy function for each level have been constructed.

25. Mass ratio of the lithium isotopes from the spectrum of Li_2. ANDREW MCKELLAR, *University of California.* (*Introduced by* R. T. BIRGE.)—The blue-green band spectrum of lithium has been photographed, in absorption, in the second order of a 21-foot grating. The (0, 0), (1, 0) and (2, 0) bands were measured and in the first two of these the branches due to the less abundant Li^6Li^7 molecule, as well as those of the Li^7Li^7 molecule were identified, extending the analyses of Harvey and Jenkins and of Wurm. By applying the least squares methods developed by Birge in his work on the oxygen isotopes, the vibrational term differences of the upper, $^1\Pi$, state were found. From these, employing the theory of the vibrational isotope effect in band spectra, the square root of the ratio of the reduced masses of the isotopic molecules, $\rho = (\mu/\mu^i)^{1/2} = \omega_e^i/\omega_e$ is found to equal 1.04103 ± 0.00018. The mass-spectrograph results of Costa, modified by Aston, give for the atomic weights of the lithium isotopes, 7.012 ± 0.002 and 6.012 ± 0.002 from which the mass ratio $Li^7/Li^6 = 1.16633$ with a *limit* of error ± 0.00051. The above value of ρ corresponds to the ratio $Li^7/Li^6 = 1.16750$ with a *probable* error ± 0.00073, giving a fairly satisfactory agreement of the two results. The latter ratio gives, assuming that $Li^6 = 6.012$, a packing fraction of 27 for Li^7, which falls directly on Aston's curve of packing fraction against mass number.

26. A new analysis of Slater's compressibility data. H. M. EVJEN, *California Institute of Technology.*—On the basis of empirical relations derived from Slater's compressibility data for the alkali halides a set of differential equations is constructed. The general solution of this set of equations is derived, whereby the most general form is obtained for the potential of repulsion. Whereas a curious and very striking agreement with Born's theory is pointed out, this theory is again repudiated by a more general argument than has heretofore appeared in the literature. By the assumption that the repulsive forces are essentially a result of an interaction along the "atomic boundaries" a unique solution is obtained by functional analysis. This solution has many interesting features and is in many respects similar to the representations of the repulsive force which have been suggested on the basis of quantum theoretical considerations.

27. On cooperative phenomena. F. ZWICKY, *California Institute of Technology.*—The study of a so far neglected type of effects, which may be called *cooperative phenomena* is proposed. It is shown that these phenomena play a great rôle in astrophysics, in the physics of solids and liquids and will probably be essential for a study of the physical characteristics of living organisms. A preliminary classification of various types of cooperative phenomena is given. As a particular case the physics of crystals is studied and the view advanced that certain cooperative phenomena are responsible for the existence of a crystalline state of matter. If this view is accepted then it follows that crystals in general possess a *secondary structure*. The experimental consequences of this conclusion are discussed.

28. The latitude effect on secondary electrons due to cosmic rays. R. M. LANGER, *California Institute of Technology.*— Two simplified problems were examined to determine whether cosmic-ray intensity measurements would be influenced by the action of the terrestrial magnetic field on secondary electrons released in the atmosphere. 1st. Electrons move with constant curvature through an atmosphere whose density varies exponentially with height. 2nd. Electrons move through a uniform atmosphere with curvature increasing as their energy decreases. The important parameters—rate of loss of energy along the path and curvature at any height in the atmosphere—are not definitely known but the conclusions are not affected by the uncertainty. It is believed that the simplifications are appropriate and do not invalidate the argument for application to the actual case. Moreover it seems that the two problems practically exhaust the possibilities for electrons generated in the atmosphere. The conclusion is that for any reasonable values of the parameters involved, no latitude effect as large as three percent is to be expected for electrons generated in the earth's atmosphere. The conclusion holds for measurements made at altitudes up to 20,000 feet at least.

29. Sound absorption in molecular gases. H. O. KNESER, *University of Marburg. Introduced by Professor L. B. Loeb.*— The present data on absorption of sound in molecular gases do not agree with the classical Kirchhoff-Stokes formula, either in the order of magnitude or in the dependence upon frequency (ν). Now that it has been established, that sound dispersion, caused by the finite duration (β) of adjustment of internal energy equilibrium, occurs at frequencies which can be realized experimentally, sound absorption can be explained in the same way. If β is of the same order of magnitude as $1/2\pi\nu$, there is a phase lag between the variation of volume and pressure, which causes an irreversible transformation of sound energy into heat. Thus, in addition to the classical absorption, we have selective absorption in nearly the same range of frequency as that in which dispersion occurs. The absorption can be calculated exactly for those gases whose dispersion curve is known (CO_2 and N_2O), and is in good agreement with the experimental data. In other cases (O_2, SO_2) β can be evaluated by fitting the absorption curve to the experimental values. Thus almost all present data can be explained within the limits of experimental error.

30. Magnetization in strong fields as a function of temperature. PAUL S. EPSTEIN, *California Institute of Technology*.—The author published recently (Phys. Rev. **41**, 91 (1932)) a theory of ferromagnetic phenomena. One of the results of this theory which is capable of experimental verification is the dependence of the limiting magnetization in strong fields on the temperature. The only empirical data which are suitable for such a comparison refer to nickel, and the region in which a good agreement can be expected is that of low temperatures. This is completely borne out by the results of the comparison: The experimental points taken from the measurement of Weiss and Forrer fall with good accuracy upon the theoretical curve up to the temperature of 400°K. For higher temperatures the theoretical values decrease much more rapidly than our theory predicts owing, presumably, to some simplifications in carrying it through which are not justified in the region of high temperatures. The characteristic temperature $\theta l = J/2k$, where J denotes an interchange integral and k Boltzmann's constant) turns out to be 400°K, in the case of nickel, about $\frac{2}{3}$ of the temperature of the Curie point (625°K) as measured empirically.

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